Prediction of Surface Flow Coefficient of Adsorbed Gases on Porous Media

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INTRODUCTION

When an adsorbable gas flows or diffuses through microporous media, the flux is appreciably increased in the presence of the adsorbed phase. This additional flow, or so-called surface flow, is important in both fundamental research and such practical applications as adsorption, catalytic reaction, gaseous separation, and drying.

The models most commonly used to describe the surface flow mechanism are the hydrodynamic model (Babbit, 1950; Gilliland et al., 1958) and the hopping model (Hill, 1956; Higashi et al., 1963; Smith and Metzner, 1964; Weaver and Metzner, 1966; Ponzi et al., 1977; Okazaki 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 these models.

Despite the famous work performed by Gilliland et al. (1974), there are still some ambiguities in predicting the surface flow coefficient. The purpose of the present work is to propose a prediction procedure of the surface flow coefficient based on the hopping model derived by the authors.

PREDICTION PROCEDURE OF SURFACE FLOW COEFFICIENT

The surface flow coefficient D_s is defined in Eq. 1.

$$N_s = -\rho_{app} D_s A dq/dl \tag{1}$$

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 BET equation

$$D_s = \frac{D_{s0}(1-x)\int_{E_{a0}^{\circ}}^{E_{a0}} \left((e^{-aE/(RT)} - e^{-E/(RT)})/\{(1-e^{-E/(RT)})\,[1-(1-x)\theta(1-\tau_1/\tau_0)]\}\right) g(E)dE}{\int_{E_{a0}^{\circ}}^{E_{a0}} g(E)dE} \tag{2}$$

where

$$\tau_1/\tau_0 = \frac{(e^{-aE/(RT)} - e^{-E/(RT)})(1 - e^{-E_{a1}/(RT)})}{(e^{-E_{s1}/(RT)} - e^{-E_{a1}/(RT)})(1 - e^{-E/(RT)})} \tag{3}$$

The values, except a and D_{s0}, in Eq. 2 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 and the temperature.

For the case where the surface flow data on a set of gas and adsorbent are obtained, the parameters a and D_{s0} in Eq. 2 can be determined from the data. The dependence of the surface flow coefficient on the amount adsorbed and the temperature can be calculated using Eq. 2. The surface flow, however, cannot be predicted from adsorption isotherms and the physical properties of the adsorbate and adsorbent without using observed data on surface flow. Therefore, it is convenient to present a simple formula for the parameters a and D_{s0}.

The value of a does not differ greatly for many experimental systems, as shown in previous papers (Okazaki et al., 1981; Tamon et al., 1981). Consequently, it can be assumed that a is independent of adsorbates and constant for all kinds of adsorbent-adsorbate systems.

The parameter D_{s0} can be expressed as follows (Okazaki et al., 1981).

$$D_{s0} = C'\delta^2/\tau_{s0} \tag{4}$$

where C' is a constant characteristic of the porous media, which is determined from the specific surface area of the porous media, the tortuosity factor of the porous media, and the geometrical configuration of the adsorption sites. δ is the distance between neighboring sites. τ_{s0} is defined as the time of oscillation of the molecules in the adsorbed state, referring especially to vibrations

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TABLE 1. PREDICTED RESULTS FOR SURFACE FLOW COEFFICIENTS

Gas	Porous Solid	$S_T \times 10^{-3}$	D_{s0}	Accuracy*	Reference	Key
C_2H_4	Vycor	117	7.47×10^{-3}	0.497	Okazaki et al. (1981)	□
C_3H_6	Vycor	117	7.47×10^{-3}	0.120	Okazaki et al. (1981)	○
iC_4H_{10}	Vycor	117	7.47×10^{-3}	0.421	Okazaki et al. (1981)	△
SO_2	Vycor	117	7.47×10^{-3}	0.398	Okazaki et al. (1981)	▽
CF_2Cl_2	Linde silica	300	1.38×10^{-2}	0.507	Carman and Raal (1951)	●
SO_2	Linde silica	300	1.38×10^{-2}	0.277	Carman and Raal (1951)	▼
CF_2Cl_2	Carbolac	960	2.95×10^{-2}	0.582	Carman and Raal (1951)	◑
CO_2	Carbolac	960	2.95×10^{-2}	0.504	Carman and Raal (1951)	◐
SO_2	Vycor	163	9.28×10^{-3}	0.357	Gilliland et al.. (1974)	▼
CO_2	Vycor	163	9.28×10^{-3}	0.268	Gilliland et al. (1974)	◓
C_3H_6	Vycor	143	8.51×10^{-3}	0.313	Gilliland et al. (1958)	▲
iC_4H_{10}	Vycor	143	8.51×10^{-3}	0.810	Gilliland et al. (1958)	◒
C_2H_6	Vycor	144	8.56×10^{-3}	0.184	Horiguchi et al. (1971)	■
C_3H_6	Vycor	144	8.56×10^{-3}	0.337	Horiguchi et al. (1971)	▲
CF_2Cl_2	Carbon Regal	106	7.00×10^{-3}	0.398	Ponzi et al. (1977)	▲
C_2H_4	Activated alumina	344	1.51×10^{-2}	0.738	Tamon et al. (1981)	◧
C_3H_6	Activated alumina	344	1.51×10^{-2}	0.668	Tamon et al. (1981)	◨
iC_4H_{10}	Activated alumina	344	1.51×10^{-2}	0.663	Tamon et al. (1981)	▼
H_2O	Activated alumina	130	8.00×10^{-3}	0.943	Toei et al. (1983)	⬓
C_3H_8	Activated carbon	1225	3.46×10^{-2}	1.410	Suzuki et al. (1983)	■
nC_4K_{10}	Activated carbon	1225	3.46×10^{-2}	0.761	Suzuki et al. (1983)	■
C_3H_6	Activated carbon	1100	3.23×10^{-2}	0.659	Asaeda et al. (1981)	◩

* Mean square deviation $= [(1/N)\Sigma(D_{sexp} - D_{scal})^2/D^2_{sexp}]^{1/2}$.

perpendicular to the surface. It can be considered that τ_{s0} is of the same order of magnitude as the time of vibration of the atoms of the adsorbents and is independent of the kind of adsorbate (de Boer, 1952). Therefore, the main controlling factors of D_{s0} seem to be the specific surface area and the tortuosity factor of the porous media, and D_{s0} is proportional to S_T/k_s^2. The tortuosity factor of the porous media k_s may be a function of the specific surface area S_T. Therefore, in the present work, D_{s0} is expressed by the following empirical equation:

$$D_{s0} = \alpha S_T{}^{\beta} \tag{5}$$

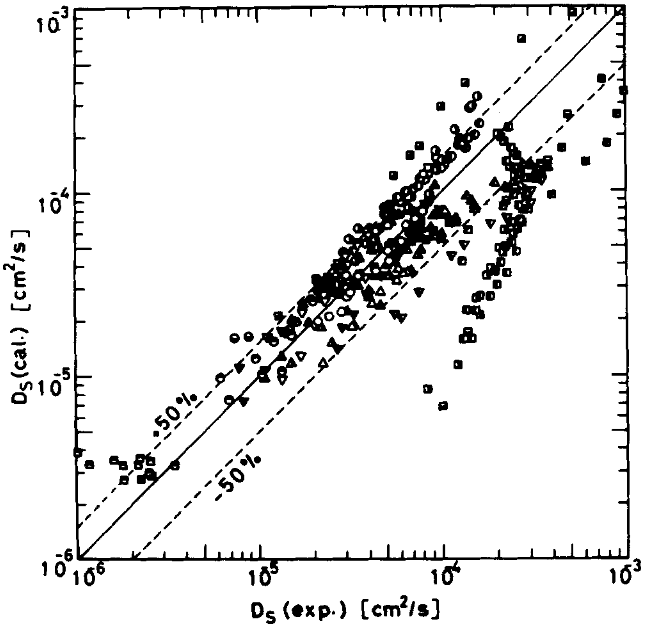

Figure 1. Comparisons of predicted and observed results. Keys are listed in Table 1. ---- calculated by $(D_{scal} - D_{sexp})/D_{sexp}$.

In order to calculate the surface flow coefficient D_{s0} by Eqs. 2 and 5, we need to know the values of a, α, and β. Using the previously published data listed in Table 1, the values of the above three parameters were obtained by the least-square method as $a = 0.49$, $\alpha = 3.65 \times 10^{-6}$, and $\beta = 0.65$. Here we adopted the surface flow data available to determine a and D_{s0} using Eq. 2. The determined value of β is smaller than 1, and this suggests that the tortuosity factor for surface flow increases with the specific surface area of the porous media.

The results predicted using the proposed procedure are shown in Figure 1. The accuracy of the prediction is also presented in Table 1. The mean square deviation for all experimental data is 55%. The rate of surface flow can be predicted by Eqs. 1, 2, and 5 using the determined values of a, α, and β.

Strictly speaking, it may be considered that the values of a, α, and β depend on the adsorbates and adsorbents. Since the constant values were obtained in this work, the method proposed here is useful in roughly predicting the surface flow rate. More investigations of a and D_{s0} will be needed to establish an accurate prediction procedure for the surface flow coefficient.

CONCLUSION

A procedure to predict the approximate value of surface flow coefficient without using surface flow data was proposed. One of the experimental constants, a, in the random hopping model was 0.49. Another constant, D_{s0}, was expressed by the following empirical function of specific surface area of porous materials:

$$D_{s0} = 3.65 \times 10^{-6} S_T{}^{0.65}$$

Although this procedure has considerable error, the surface flow coefficient can be roughly predicted.

NOTATION

A = cross-sectional area of porous material, cm^2
a = parameter defined in Eq. 2
C' = constant defined in Eq. 4
D_s = surface flow coefficient, $cm^2 \cdot s^{-1}$
D_{s0} = parameter defined in Eq. 2, $cm^2 \cdot s^{-1}$
E = adsorption energy, $kJ \cdot mol^{-1}$
E_{a0} = differential heat of adsorption, $kJ \cdot mol^{-1}$
E_{al} = heat of vaporization, $kJ \cdot mol^{-1}$
E_{s1} = activation energy for migration in all layers above the first layer, $kJ \cdot mol^{-1}$
$g(E)dE$ = number of molecules adsorbed which have the heat of adsorption between E and $(E + dE)$
k_s = tortuosity factor for surface flow
l = dimension along axis, cm
N_s = rate of surface flow, $mol \cdot s^{-1}$
p = pressure, kPa
p_s = saturated vapor pressure, kPa
q = amount adsorbed, $mol \cdot kg^{-1}$
q_m = monolayer amount adsorbed, $mol \cdot kg^{-1}$
R = gas constant, $J \cdot K^{-1} \cdot mol^{-1}$
S_T = specific surface area, $m^2 \cdot kg^{-1}$
T = temperature, K
x = relative pressure, p/p_s

Greek Letters

α = parameter defined in Eq. 5
β = parameter defined in Eq. 5
δ = distance between adsorption sites, cm
θ = surface coverage, q/q_m
ρ_{app} = apparent density of porous material, $kg \cdot m^{-3}$
τ_0 = mean holding time for migration in first layer, s
τ_1 = mean holding time for migration in all layers above the first layer, s
τ_{s0} = time of oscillation of adsorbed molecules, s

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