Concentration Dependence of Surface Diffusion Coefficient of Propionic Acid in Activated Carbon Particles

A Wicke Kallenbach type steady state diffusion experiment was performed for varying concentrations of propionic acid solution through activated carbon pellets. Since surface diffusion is a dominant mechanism, concentration dependence of the surface diffusion coefficient is precisely determined from the change of diffusion flux with concentration. Strong dependence of surface diffusion coefficient on amount adsorbed is partially interpreted in terms of the change of heat of adsorption with surface coverage as determined from separate equilibrium runs.

MOTOYUKI SUZUKI and
TAKAO FUJII

Institute of Industrial Science,
University of Tokyo
Tokyo 106 Japan

SCOPE

It is well established that intraparticle diffusion is one of the most significant rate determining steps during aqueous phase adsorption of organic materials on activated carbon pellets. Recently, it has been pointed out that surface diffusion, i.e., migration of the adsorbed organics on adsorption surface, plays a more important role in pores than ordinary molecular diffusion when organics are low molecular volatile species.

The kinetics of surface diffusion, however, have not been yet clarified in aqueous phase adsorption, since only a limited amount of experimental data has been given in the literature. As is already known for surface diffusion in the gaseous phase, the surface diffusion coefficient in aqueous phase adsorption is expected to be highly dependent on the amount adsorbed.

In order to clarify the phenomenon, a steady state experiment is essential since, by this means, the measured diffusion coefficient is free from a change in amount adsorbed during the run. A steady state experiment in the aqueous phase, however, is accompanied by the difficulty that each run takes a long time, sometimes several hundred hours to reach steady state. Controlling the experimental system is thus not easy and needs careful management for reproducible results.

CONCLUSIONS AND SIGNIFICANCE

The steady state technique for determining dependence of the surface diffusion coefficient on the amount adsorbed was proposed here and proved to be useful. The magnitude of the surface diffusion coefficient increases almost ten times when the amount adsorbed increases from 0.2 to 0.8 mol/kg, and also about 2.5 times when temperature is raised from 293 to 313 K.

From a separate set of experiments, adsorption equilibrium relations were determined by batch adsorption at 283, 293, 303 and 313 K for a wide range of concentration from 3×10^{-3} to 20 mol/m^3. The results showed that the apparent isosteric heat of adsorption $Q_{st,a}$, determined from van't Hoff plotting of the experimental data, decreases with the amount adsorbed q(mol/kg) as

$$Q_{st,a} = -Q_0 \ln (a \cdot q) = -7.03 \times 10^3 \cdot \ln (0.045\, q) (\mathrm{J/mol}) \quad (11)$$

for $q > 0.07$ mol/kg and

$$Q_{st,a}\big|_{q=0} = 4.56 \times 10^{-4} (\mathrm{J/mol})$$

The relation given above is in consistence with the fact that above $q > 0.1$ mol/kg, each isotherm can be correlated by Freundlich type equation $q = k \cdot C^{1/n}$ and n is related to the value of Q_0 in Eq. 11 by $n = Q_0/RT$. Equation 11 is also applied for interpreting the dependence of D_s. The activation energy of surface diffusion in the present system is almost the same order of magnitude as Q_{st}. Using Eq. 11 in an Arrhenius type equation gives

$$D_s = D_{so}(a \cdot q)^n \quad (17)$$

This equation with arbitrary choice of $D_{so} = 1.5 \times 10^{-6}$ m^2/s falls close to the measured results but the dependence of D_s on q is not fully accounted for.

INTRODUCTION

Surface diffusion becomes dominant in the adsorption of volatile organic component from aqueous solution onto activated carbon particles. The author (1975) showed that the effective surface diffusion coefficient, D_s, is dependent on the nature of the adsorbate and gave a correlation of D_s vs. the ratio of adsorption temperature, T, to boiling temperature, T_b, of the adsorbate:

$$D_s = 1.1 \times 10^{-8} \exp (-5.32\, T_b/T) \quad (1)$$

Surface diffusion is known also to be highly dependent on the amount adsorbed (or surface coverage) as has been discussed for gaseous systems by Gilliland et al. (1958, 1974), Higashi et al. (1963) and Roybal and Saunders (1972). Regarding aqueous phase adsorption, however a lack of adsorption rate data has retarded the elucidation of adsorption kinetics. Komiyama and Smith (1974) related the surface diffusion coefficient to the adsorption equilibrium constant for adsorption of benzaldehyde from methanol-water mixtures. Neretnieks (1976) interpreted the data of Fritz and Spahn and Shlünder in terms of the change of heat of adsorption

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on the basis of a hypothetical modified Temkin isotherm. Sudo (1978) measured batch adsorption of chlorophenols, chloroplatinic acid and benzoic acid on activated carbon from several initial concentrations and found that the surface diffusion coefficient, D_s, can be correlated as

$$D_s = D_s^* \exp(0.88 \cdot q_f) \qquad (2)$$

where q_f is the final amount adsorbed in mol/kg. Those discussions are based on experimental determinations of D_s which were measured by means of transient techniques such as batch adsorption or a breakthrough technique and thus were complicated by the change of amount adsorbed during the experiment.

The purpose of the present study is to clarify experimentally the dependence of D_s on amount adsorbed, q, by steady state measurement and to compare the results with the dependence of isosteric adsorption energy on q as determined from separate equilibrium experiments for aqueous phase adsorption of propionic acid on activated carbon.

EXPERIMENTAL

Materials. The adsorbent is a commercial activated carbon, HGR 513, extruded cylindrical pellet of 4×10^{-3} m in diameter and 5×10^{-3} m in length, supplied by Takeda Yakuhin Co.; its specific nitrogen surface area is 1.225×10^6 m^2/kg. The pellet density, 0.72×10^3 kg/m^3. Macropore volume of the pellet is given as 0.40×10^{-3} m^3/kg, while that of micropore (radius smaller than 10^{-8} m) determined by nitrogen adsorption at liquid nitrogen temperature is 0.46×10^{-3} m^3/kg, resulting in the total prosity of 0.62(−). Propionic acid is research grade obtained from Wako Chemical Co.

Isotherm Experiment. Adsorption isotherms were determined by contacting a volume V (2×10^{-4} m^3) of solution of known concentration, C_o, with a mass W_s ($0.3 \sim 3 \times 10^{-3}$ kg) of adsorbent in 3×10^{-4} m^3 pyrex flask with ground stopper. Prior to contacting, solution in the flask and adsorbent were steam autoclaved to avoid biological contamination.

The flasks were shaken with a reciprocating shaker thermostated to within ±0.1 K at 283, 293, 303 and 313 K.

The time required to reach equilibrium was more than 150 h since the size of adsorbent was rather large.

Final concentration, C, was then analyzed by gas chromatography. Concentrations as low as 0.2×10^{-3} kg/m^3 (2.4×10^{-3} mol/m^3) were possible to determine by Okura gas chromatography with steam carrier and a flame ionization detector. A 1.0 m L and 3×10^{-3} m i.d. glass column packed with kieselguhr support particles (80/100 mesh) loaded with phospheric acid was used at 423 K.

Standard solutions of several different concentrations were prepared to calibrate peak heights for each analysis. At least three repeated injections were necessary to obtain a reliable result for each sample.

Amount adsorbed q which is in equilibrium with C, was calculated by

$$q = \frac{V}{W_s}(C_0 - C) \qquad (3)$$

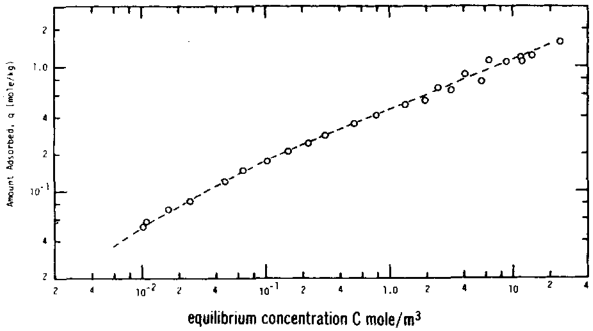

Figure 1. Adsorption isotherm of propionic acid on activated carbon HGR 513 from aqueous solution measured at 303 K.

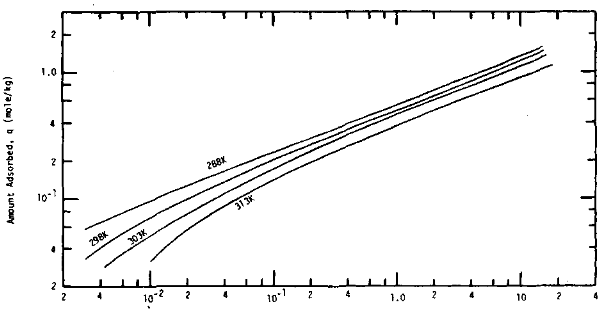

Figure 2. Summary of adsorption isotherms of propionic acid on activated carbon at 283, 293, 303 and 313 K.

Typical of the measured equilibrium results, q vs. C at 303K is shown in Figure 1, where a dashed regression line is included. Figure 2 summarises the results for the four adsorption temperatures; only the regression lines are shown.

Diffusion Experiment. A steady state diaphragm cell method was adopted. This method originally proposed by Wicke and Kallenbach (1941), is often used for diffusion studies in gaseous phase but no work has been reported for liquid phase studies. The cell was made out of teflon block, the dimensions of which are given in Figure 3. The diaphragm is made of 4.0×10^{-3} m stainless steel plate in which 24 holes, 4.0×10^{-3} m in diameter, are drilled. In each hole an activated carbon pellet was fixed by epoxy cement which was viscous enough not to penetrate into the pores of particles. After the cement became solidified, the carbon particles were carefully shaped with knife and emery paper so that each side of the diaphragm became a smooth flat surface. Thus the area effective for diffusion is 3.02×10^{-4} m. The volume of each side of the cell is 5.6×10^{-5} m^3 and a teflon disk rotor with magnet fixed on it is put in each cell. The rotor is spun by an external rotating magnet. This provided good contact between carbon and liquid by minimizing the mass transfer resistance on the diaphragm, and also the disks were effective in minimizing the liquid volume in the cell. A schematic flow sheet of the experimental apparatus is shown in Figure 4. Special care was taken to avoid a pressure difference across the diaphragm so that the flow of solution across the particle is negligible. This is accomplished by keeping the horizontal liquid level at the outlets equal and by careful control, keeping the flow rate to both sides equal and constant. The cell was

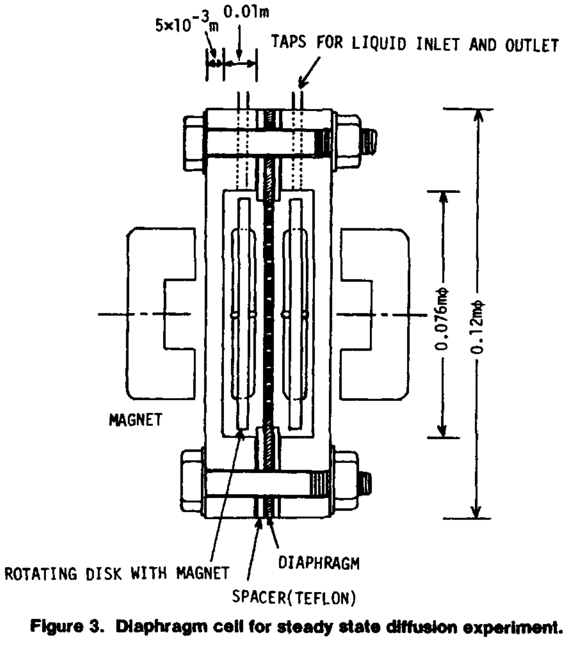

Figure 3. Diaphragm cell for steady state diffusion experiment.

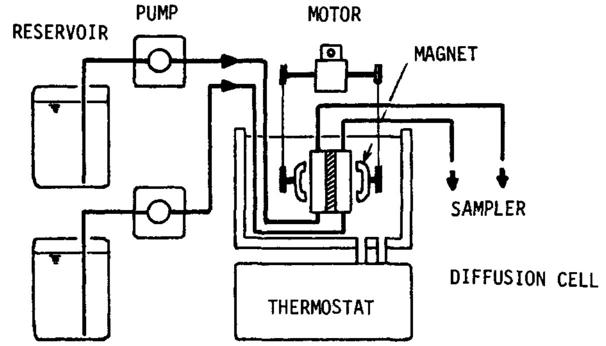

Figure 4. Schematic illustration of experimental apparatus.

placed in a constant temperature water bath and kept at 293, 303 or 313 K. Concentration of the lower concentration cell C_L, was measured daily by gas chromatography. It took more than a hundred hours for the concentration to become steady even at the highest temperature (313K) as shown in Figure 5.

C_L was kept lower than 1% of the concentration in the higher concentration side, C_H, by adjusting the flow rate of the distilled water. From the flow rate through the cell, V_L and C_L, total diffusion flux through the diaphragm, N_AS, was calculated as $N_AS = V_L \cdot C_L$. Figure 6 shows N_AS versus the amount adsorbed q_H, which is in equilibrium with C_H concentration, in the cell where propionic acid solution flows.

It should be added that by proper assumption such as microparticle size $d = 3.3 \times 10^{-6}$ m and macropore void fraction $\epsilon_a = 0.29[-]$, the maximum possible pressure difference between both sides of the cell, $\Delta P = 1 \times 10^{-3}$ m $H_2O = 9.8 \times 10^3$ P_a, gives an estimate of total flow rate of water across the diaphragm by the equation derived by Carman (1937) as 2.2×10^{-9} m^3/s. This flow gives maximum possible flux of propionic acid (e.g., $C_H = 0.04$ kg/m^3) of 8.8×10^{-11} kg/s or 5.3×10^{-9} kg/min, which is less than 1% of N_AS measured here. Hence flow across the diaphragm is assumed to have negligible effect on the diffusion results.

Reduction of Diffusion Data. At steady state, the flux of adsorbate is constant throughout the diaphragm and the following Fickian equation holds.

$$N_A = \rho_p D_s(q) \cdot \frac{\partial q}{\partial X} + D_p \frac{\partial C}{\partial X} \tag{4}$$

where $D_s(q)$ is the effective surface diffusion coefficient which is a function of the local amount adsorbed q. The second term on the Right-Hand-Side of Eq. 4 gives the contribution of molecular diffusion in the pore. The magnitude can easily be estimated since D_p is considered to be about one tenth of molecular diffusivity of propionic acid in water. It is found to be less than 5% of total diffusion flux.

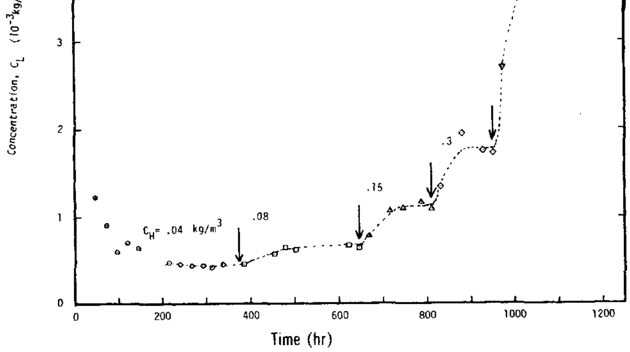

Figure 5. Observed concentration, C_L, in lower concentration cell.

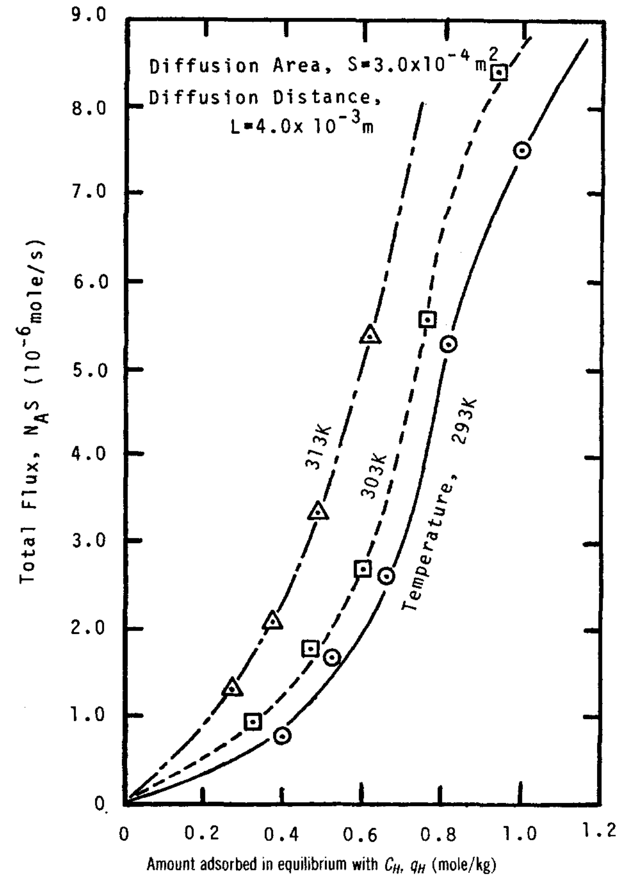

Figure 6. Diffusion flux, N_AS, calculated from C_L against adsorbed, q_H, in equilibrium with C_H.

As a first approximation, integration of Eq. 4 by neglecting the second term of R.H.S. gives

$$N_A = \frac{\rho_p}{L} \int_{q_L}^{q_H} D_s(q)dq \tag{5}$$

where L is thickness of the diaphragm and q_H and q_L correspond respectively to the amounts adsorbed in equilibrium with C_H and C_L. By adjusting the flow rate so that C_L was kept far smaller than C_H, N_A is assumed to be a function only of q_H. Then concentration dependency of D_s can be determined as

$$D_s(q) = \frac{L}{\rho_p} \{dN_A(q_H)/dq_H\} \tag{6}$$

By applying Eq. 6 to the smoothed results of N_A vs. q_H as is shown in Figure 6, D_s is obtained as a function of q as illustrated in Figure 7.

RESULTS AND DISCUSSIONS

Isotherm Results

From Figure 2, almost straight relations can be established for the results for $q > 1.5$ mol/kg, while deviations are observed at lower amount adsorbed. The Radke-Prausnitz equation can accomodate this functioned form without unnecessary complication of the formula

$$q = \frac{1}{\dfrac{1}{KC} + \dfrac{1}{kC^{1/n}}} \tag{7}$$

By determining k and n from the straight line portion ($q > 1.5$ m mol/g), K is obtained so that the curve given by Eq. 7 gives a best fit to the experimental data for lower concentrations. The thus determined k, n and K values are summarized in Table 1. Though

TABLE 1. CONSTANTS OF FREUNDLICH TYPE EQUATION $q = k\,c^{1/n}$ APPLIED TO THE ISOTHERM RESULTS FOR $q > 10^{-1}$ MOLE/KG.

Temperature (K)	k	n	Qo/RT
283	0.55	2.74	3.00
293	0.49	2.64	
303	0.43	2.52	
313	0.32	2.45	2.71

it should be noted that the values of K obtained here have some degree of ambiguity since it was not possible to determine the isotherm results for low enough concentrations, these values are used here to define the isosteric heat of adsorption Q_{st} that corresponds to zero surface coverage ($q = 0$). As determined from a van't Hoff plot (Eq. 8) $Q_{st,0} = 4.56 \times 10^4$ J/mol, Figure 8.

$$Q_{st,0} = R \cdot \frac{d \ln K}{d(1/T)} \tag{8}$$

Similarly Q_{st} for $q = 0.07$, 0.1, 0.3, 0.5, 0.7 and 1.0 mol/kg are determined from Figure 2 by using the isosteric equation:

$$Q_{st,a} = R \cdot \left.\frac{d \ln C}{d(1/T)}\right|_q \tag{9}$$

Isosteres given in Figure 9 provide $Q_{st,a}$ as a function of q as illustrated in Figure 10.

The apparent heat of adsorption in aqueous adsorption, $Q_{st,a}$, is a resultant of net heat of adsorption, $Q_{st,\text{net}}$, heat of solution, ΔH_{sol}, and heat of adsorption of water, Q_h.

$$Q_{st,a} = Q_{st,\text{net}} - \Delta H_{\text{sol}} - nQ_h \tag{10}$$

where exchange of n moles of water molecule per unit mole of propionic acid at the adsorption site is assumed. Since ΔH_{sol} of propionic acid is 2.21×10^3 J/mol and Q_h should be negligible, $Q_{st,\text{net}}$ is considered 2.21×10^3 J/mol larger than $Q_{st,a}$ and thus given in Figure 10 by broken line.

Heat of vaporization of propionic acid is given as $\lambda_{\text{vap}} = 2.85 \times 10^4$ J/mol and then $Q_{st,\text{net}}$ lies between 1.5 and 0.8 times λ_{vap}, which seems quite reasonable.

Also $Q_{st,\text{net}}$ decreases with increasing amount adsorbed and can be correlated by the equation

$$Q_{st,a} = -Q_0 \ln (a \cdot q) \tag{11}$$

where $a = 0.045$ kg/mol, and $Q_0 = 7.03 \times 10^3$ J/mol, or

$$q = 22.0 \exp\left(-\frac{Q}{Q_0}\right) \tag{12}$$

for 0.07 mol/kg $< q <$ 1.0 mol/kg.

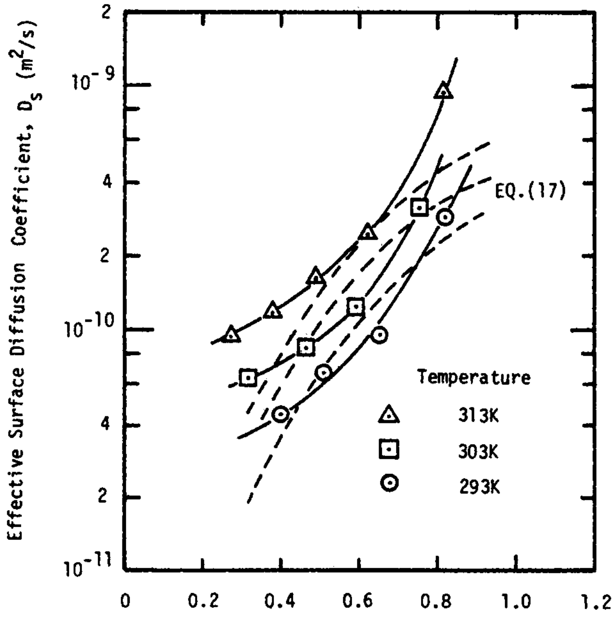

Figure 7. Surface diffusion coefficient plotted against amount adsorbed.

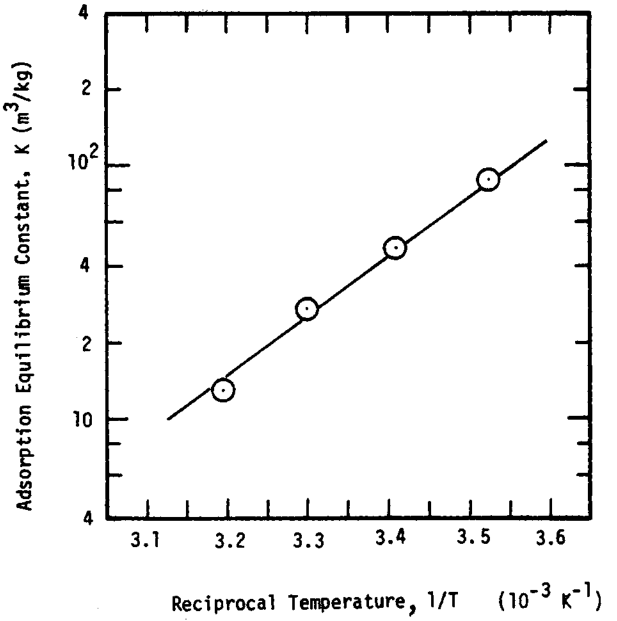

Figure 8. Van't Hoff plot of adsorption equilibrium constant, K.

This apparent decrease of heat of adsorption is in line with the Freundlich type adsorption isotherms higher coverages as already given by Halsey (1974). In the case the classical treatment of het-

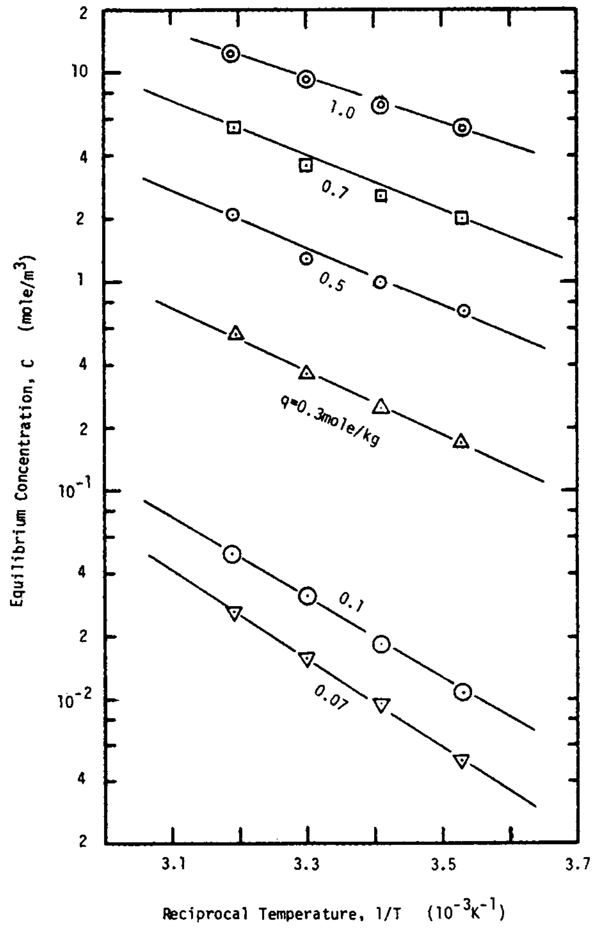

Figure 9. Adsorption isosteres for determining isosteric heat of adsorption from Eq. 9.

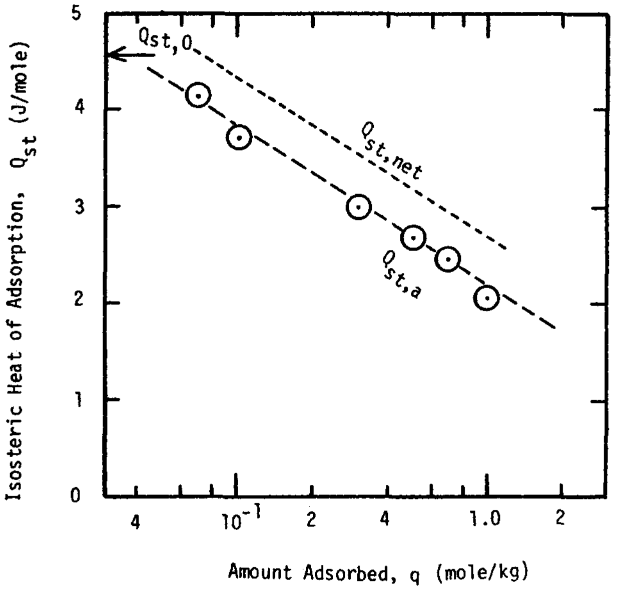

Figure 10. Isosteric heat of adsorption $Q_{st,a}$ plotted against amount adsorbed q.

erogeneous surfaces is applicable, the Freundlich constant $1/n$ is related to Q_0 defined by Eq. 11 or 12, as

$$\frac{Q_0}{RT} = n \tag{13}$$

Q_0/RT's were calculated for 283 and 313 K and are included in Table 1. Fair agreement between the n obtained from the experiment and Q_0/RT does not necessarily justify the classical assumption of energy distribution on the surface as given by Eq. 11, at this stage. Further accumulation of experimental isotherm at several temperatures might be helpful in establishing isotherm relations in aqueous phase adsorption.

Surface Diffusion Coefficient

From Figure 7, D_s is obviously a strong function both of temperature and of amount adsorbed. Regarding temperature dependence, the Arrhenius plots of D_s for several levels of q are illustrated in Figure 11. The plots give activation energies, E_a, that correspond for $q = 0.3$, 0.5 and 0.7 mol/kg to 3.8, 3.6 and 3.2 × 10^{-4} J/mol. These figures are of the same order of magnitude as the isosteric heat of adsorption.

$$E_a \simeq Q_{st} \tag{14}$$

For the variation of D_s with the amount adsorbed given in Figure 11, change of activation energy with increasing q may be used to explain the results as was done by Gilliland (1974). Defining D_s in an ordinary form as

$$D_s = D_{so} \exp(-E_a/RT) \tag{15}$$

and combining Eqs. 11, 14, and 15, D_s becomes

$$D_s = D_{so} \exp\left\{-\frac{Q_0}{RT} \ln(a \cdot q)\right\} \tag{16}$$

Finally by introducing Eq. 13 into Eq. 16, we get

$$D_s = D_{so}(a \cdot q)^n \tag{17}$$

An arbitrary choice for D_{so} of 1.5 × 10^{-6} m^2/s Eq. 17 gives estimates of D_s with q as shown by the dotted lines in Figure 7 where the n of Table 1 and $a = 0.045$ kg/mol are used. Equation 17 gives a somewhat different tendency for the change of D_s with increasing q, which suggests that the variation of Q_{st} with q is probably not the only explanation of the large increase of D_s with amount adsorbed.

Further accumulation of precise measurements of D_s as well as isotherms at different temperature levels for many systems is needed for more detailed understanding of the mechanism of surface diffusion in aqueous phase adsorption.

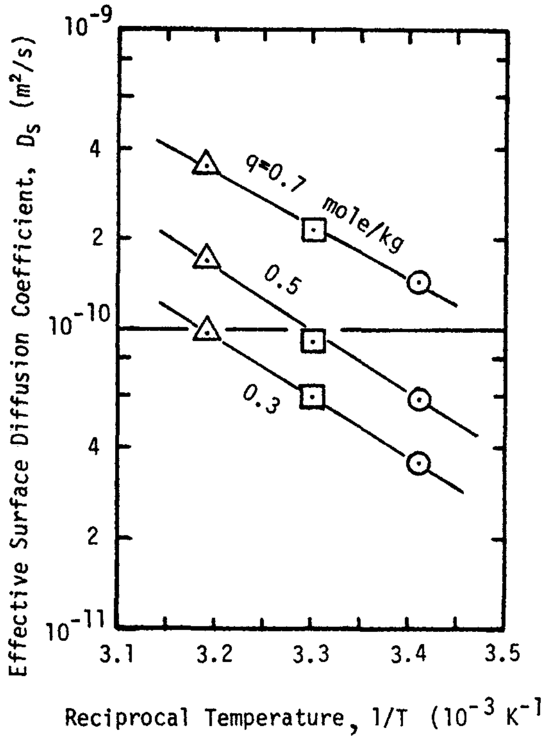

Figure 11. Arrhenius plot of surface diffusion coefficient D_s.

NOTATION

a = constant defined by Eq. 11, kg/mol
C = concentration in the bath, mol/m
C_H, C_L = concentrations of the solutions in the both sides of the cell, mol/m^3
C = initial concentration, mol/m^3
D_s = effective surface diffusion coefficient, m^2/s
D_s^* = D_s for $q = 0$ in Eq. 2, m^2/s
E_a = activation energy, J/mol
H_{sol} = heat of solution, J/mol
K = constant defined in Eq. 7, m^3/mol
k = constant defined in Eq. 7
L = thickness of the pellet, mol/m^2
N_A = flux density of propionic acid, kg/m^2 · s or kg/m^2 · min
n = constant in Freundlich equation
Q_h = heat of adsorption of water molecule, J/mol
Q_0 = constant defined by Eq. 11, J/mol
Q_{st} = isosteric heat of adsorption, J/mol
q = amount adsorbed, mol/kg
q_f = final amount adsorbed, mol/kg
q_H, q_L = amount adsorbed in equilibrium with solutions in the both sides of the cell, mol/kg
S = cross-sectional area effective for diffusion, m^2
T = adsorption temperature, K
T_b = boiling point of an organic substance, K
V = volume of the bath, m^3
V_L = flow rate of distilled water measured at outlet of the cell, m^3/s
W_s = weight of adsorbent, kg
X = diffusional distance in pellet, m
λ_{vap} = heat of vaporization, J/mol
ρ_p = particle, density, kg/m^3

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Numerical Solution for the Flow of Highly Viscous Fluid in Agitated Vessel with Anchor Impeller

Fluid motion in an agitated vessel with an anchor impeller is characterized by flow in a horizontal plane induced by the vertical arms of the impeller rotating near the vessel wall. A numerical algorithm of the two-dimensional flow in the horizontal plane is established using an iterative method for the determination of the boundary values of stream function. The computational results of the velocity profiles and agitation power are compared with those of the experiments, and it is shown that the numerical method used in this study is very useful to analyze the flow past the vertical arms of an anchor impeller.

M. KURIYAMA, H. INOMATA,
K. ARAI, and S. SAITO
Department of Chemical Engineering
Tohoku University
Sendai, Japan 980

SCOPE

The anchor agitator has a simple and basic configuration suited for agitation of a highly viscous fluid, and is widely used in the chemical and food industries. Analysis of the flow around the vertical blades of an anchor impeller provides significant information on agitation with close-clearance impellers regarding power consumption and mixing and heat transfer performance. Although some experimental studies on flows in the region of anchor impeller blades have been reported (Peters and Smith, 1967, 1969; Murakami et al., 1972), it seems to have been difficult for these experimental studies to give detailed information on flow characteristics such as shear rate distribution, which is usually obtained by differentiating experimental data.

In this respect, numerical study may be significant even if some simplification of a flow field is required to solve a flow problem numerically. However, although laminar, the flow in an anchor-agitated vessel has attracted very few numerical studies. This paucity may mainly be attributed to the existence of plural solid boundaries because while one of the boundary values of the stream function can be prescribed in advance the others must be determined through a computational procedure. Hiraoka et al. (1978) solved numerically two-dimensional flow problems in the horizontal plane of a paddle-agitated vessel with two solid boundaries, i.e., the surfaces of the agitator and of the vessel wall, applying the conservation law of angular momentum. However, no realistic, accurate and stable solution seems yet to have been given for a flow restricted by more than two solid boundaries in a vessel, such as in an anchor-agitated vessel, which has boundaries on the shaft, blades and vessel wall.

Recently, Daiguji and Kobayashi (1979) gave a numerical solution for the two-dimensional flow in channels past two solid bodies and proposed an iterative method for the determination of the boundary values of the stream function by use of the fact

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Correspondence concerning this paper should be addressed to S. Saito.

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