

SURFACE DIFFUSION COEFFICIENT IN AQUEOUS PHASES ADSORPTION ON MACRORETICULAR ADSORBENTS

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Recently, the authors reported that liquid-phase adsorption equilibria of phenols on macroreticular polymeric adsorbents (MR resins) such as Amberlite XAD-4 and XAD-7 were satisfactorily represented, over a wide range of concentration, by the equation of Jossens *et al.*, derived thermodynamically on the basis of a heterogeneous surface adsorption theory.²⁾ The equation has three parameters, H , K and p :

$$c = (q/H) \exp(Kq^p) \quad (1)$$

where c is the equilibrium concentration of solute and q is the amount adsorbed. The pre-exponential parameter H corresponds to the Henry's law constant and relates to the maximum isosteric heat of adsorption, E_0 . This equation postulates the following relation between the isosteric heat of adsorption, E , and q .

$$E_0 - E = Cq^p \quad (2)$$

where C is a constant related to the parameter K .

Concerning transport of solutes within liquid-filled pores of MR resins, Komiyama and Smith have reported that the intraparticle diffusion of benzaldehyde includes a contribution of surface diffusion as well as of pore-volume diffusion,³⁾ and that the values of surface diffusivity, D_s , were correlated to the adsorption equilibrium constants of benzaldehyde,⁴⁾ though their experiments were carried out only for dilute solutions. Van Viet *et al.* analyzed the adsorption rate of phenol from aqueous solutions on MR resins, taking into account only the effective surface diffusion.⁹⁾

The intraparticle diffusion of organics in dilute aqueous solutions on activated carbons has been widely investigated. In most cases, the surface diffusion is considered to be much more important than the pore-volume diffusion, and the experimental data on adsorption rate have been analyzed by assuming that D_s is constant during the course of a finite batch

adsorption experiment. The values of D_s thus obtained were correlated as a function of the final equilibrium amount absorbed, q_∞ , as in the following equation.^{7,10)}

$$D_s = D_s^0 \exp(k \cdot q_\infty) \quad (3)$$

Such dependence has been explained by a decrease in adsorption energy with an increase in q .⁵⁻⁸⁾

In the case of liquid-phase adsorption of organics on MR resins, however, the dependence of D_s on q has not been investigated to our knowledge. The objects of this study were to investigate the dependence of D_s on q for the adsorption of phenols on XAD-4 and XAD-7 from aqueous solutions, and to find the relationship between D_s and E by the use of Eq. (2).

1. Experimental

Amberlite XAD-4 and XAD-7 were used after washing by the method described previously.²⁾ Phenol, *p*-chlorophenol, *p*-cresol and *p*-nitrophenol were used as adsorbates after purifying by ordinary methods.

Experimental procedures and the method of analysis of results were similar to those described by Komiyama and Smith.^{3,4)} The only difference in the present work is in the adsorption isotherm expression, where the Freundlich equation is replaced by the equation of Jossens *et al.* for better agreement with experimental data and for further analysis of results.

2. Results and Discussion

The pore-volume diffusivities, D_p , of phenols were determined as follows. The adsorbed amounts of phenol on XAD-4 and XAD-7 from methanol solutions were very small and were represented by Henry-type linear isotherm equations. In this case, the contribution of surface diffusion to overall intraparticle diffusion could be neglected. Therefore, from dynamic desorption experiments for the phenol-methanol system by use of a batch-type stirred-tank adsorber, the values of the ratio of porosity to

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tortuosity factor, ε_p/γ , were found to be 0.174 ± 0.015 for XAD-4 and 0.337 ± 0.026 for XAD-7, respectively. These values were close to the 0.163 and 0.414 reported for the benzaldehyde-methanol-XAD-4 and -XAD-7 systems, respectively.^{3,4)} The D_p values for the adsorption of phenols from aqueous solutions were calculated from Eq. (4), using these values of ε_p/γ and molecular diffusivities of each solute in water, D_{mw} .

$$D_p = (\varepsilon_p/\gamma) D_{mw} \quad (4)$$

Dynamic adsorption experiments were carried out for aqueous solutions of phenols. The change of amount adsorbed with time was measured for comparison with the predicted curves with known values of D_p and arbitrary values of D_s , and the values of D_s were determined by the curve-fitting method. The values of D_s thus determined are plotted against q in Fig. 1, where the final equilibrium amounts adsorbed were adopted as the q values. D_s increased with an increase in q . For activated carbons, it has been reported that the dependence of D_s on q is represented by Eq. (3) as mentioned above.^{7,10)} However, this is not the case for the present result, as can be seen from Fig. 1.

The surface diffusivity was represented by Eq. (5).

$$D_s = D_{s0} \exp(-E_a/RT) \quad (5)$$

where E_a is the activation energy for surface diffusion. Moreover, it was suggested that the activation energy E_a for surface diffusion was a fraction of adsorption energy E .¹⁾

$$D_s = D'_{s0} \exp(-\alpha E/RT) \quad (6)$$

where α is a parameter which relates to the activation energy for surface diffusion. Figure 2 shows the dependence of D_s on E , where the values of E were calculated from Eq. (2) with known values of the parameters.²⁾ The linear relationship between $\ln D_s$ and E/RT expressed by Eq. (5) was applicable to both XAD-4 and XAD-7. The Arrhenius plots of the pre-exponential factor, D'_{s0} , are shown in Fig. 3. Thus, D_s was represented by the following equations.

$$D_s = 4.31 \times 10^{-3} \exp(-44.4/RT) \exp(-0.394E/RT) \quad (7)$$

for XAD-4

$$D_s = 7.24 \times 10^{-7} \exp(-22.6/RT) \exp(-0.608E/RT) \quad (8)$$

for XAD-7

The values of 0.394 and 0.608 were the average values of α values determined at three temperatures for two types of resins, respectively, since it is considered that the α value is independent of temperature.

This result indicates that the activation energy E_a for the surface diffusion is expressed by the equation

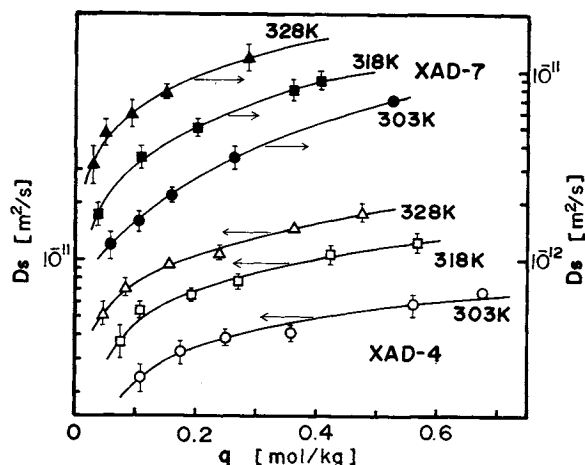


Fig. 1. Adsorbed-amount dependence of surface diffusivity of phenol.

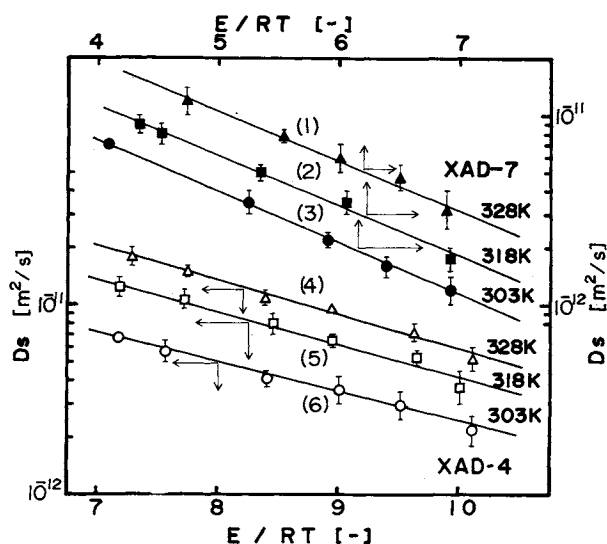


Fig. 2. Adsorption energy dependence of surface diffusivity of phenol.

- (1) $D_s = 1.86 \times 10^{-10} \exp(-0.576E/RT)$,
- (2) $D_s = 1.33 \times 10^{-10} \exp(-0.617E/RT)$,
- (3) $D_s = 9.28 \times 10^{-11} \exp(-0.632E/RT)$,
- (4) $D_s = 3.66 \times 10^{-10} \exp(-0.413E/RT)$,
- (5) $D_s = 2.28 \times 10^{-10} \exp(-0.400E/RT)$,
- (6) $D_s = 9.63 \times 10^{-11} \exp(-0.368E/RT)$.

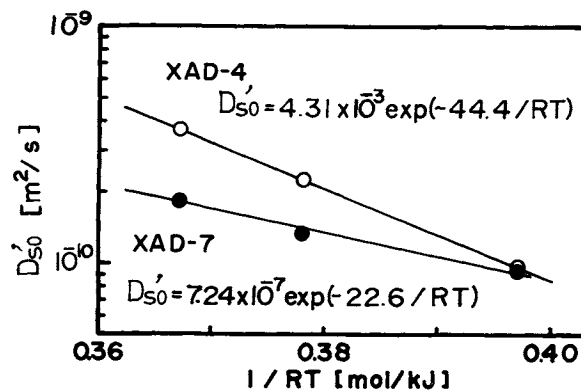


Fig. 3. Temperature dependence of D'_{s0} .

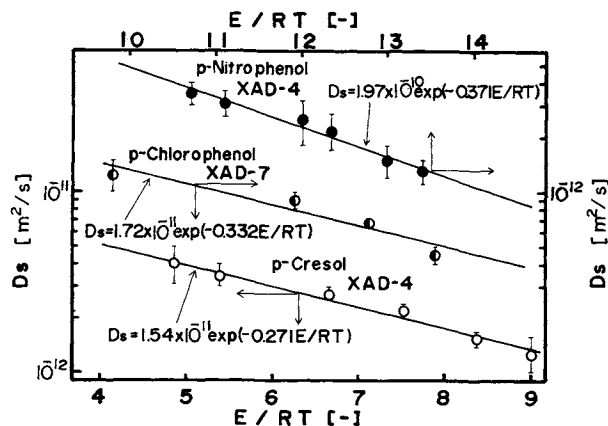


Fig. 4. Adsorption energy dependence of surface diffusivity of *p*-nitrophenol, *p*-chlorophenol and *p*-cresol.

$$E_a = \beta + \alpha E \quad (9)$$

and that the surface diffusivity is represented by Eq. (10).

$$D_s = D_{s0} \exp\{-(\beta + \alpha E)/RT\} \quad (10)$$

In this equation, β might represent the contribution of a hole-making step and αE might represent the contribution of a jumping step, if the concept of molecular diffusion in liquids is applied to the surface diffusion.⁴⁾ In the present results, the activation energy of the hole-making step (β) was much larger than that of the jumping step (αE). Moreover, the surface of XAD-7 is more hydrophilic than that of XAD-4. Hence, in the case of XAD-7, a water molecule is more strongly adsorbed on the surface and more energy is required to produce a vacant site. However, the value of β is smaller for XAD-7 than for XAD-4. Therefore, the present experimental results are not well explained by the concept of surface diffusion proposed by Komiyama and Smith.⁴⁾ Although these results are very interesting, a reasonable explanation cannot be offered at the present time.

For other solutes, Eq. (6) is also applicable, as shown in Fig. 4.

As mentioned above, D_s was determined on the assumption that D_s was constant during the course of finite batch adsorption and was correlated to the heat of adsorption according to Eq. (6).

Nomenclature

C	= coefficient related to the energy distribution of sites on the surface in Eq. (2)	$[\text{kJ kg}^p/\text{mol}^{p+1}]$
c	= bulk concentration	$[\text{mol/m}^3]$
D_{mw}	= molecular diffusivity of phenol in water	$[\text{m}^2/\text{s}]$
D_p	= pore-volume diffusivity	$[\text{m}^2/\text{s}]$
D_s	= surface diffusivity	$[\text{m}^2/\text{s}]$
D_s^0	= surface diffusivity at zero coverage	$[\text{m}^2/\text{s}]$
D_{s0}	= pre-exponential factor in Eq. (5)	$[\text{m}^2/\text{s}]$
D_{s0}^0	= pre-exponential factor in Eq. (6)	$[\text{m}^2/\text{s}]$
E	= isosteric heat of adsorption	$[\text{kJ/mol}]$
E_a	= activation energy for surface diffusion	$[\text{kJ/mol}]$
E_0	= isosteric heat of adsorption at infinite dilution	$[\text{kJ/mol}]$
H	= Henry's law constant	$[\text{m}^3/\text{kg}]$
K	= parameter in Eq. (1)	$[(\text{kg/mol})^p]$
k	= constant defined by Eq. (3)	$[\text{kg/mol}]$
p	= parameter related to the distribution of energy sites on the surface in Eq. (2)	$[-]$
q	= amount adsorbed	$[\text{mol/kg}]$
q_∞	= equilibrium amount adsorbed in finite batch adsorption	$[\text{mol/kg}]$
α	= constant related to the activation energy for surface diffusion	$[-]$
β	= constant related to the activation energy for surface diffusion	$[\text{kJ/mol}]$
ε_p	= porosity of wet particles	$[-]$
γ	= tortuosity factor	$[-]$

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