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Adsorption Mechanism of Iodine on Activated Carbon

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Abstract

The characteristics and mechanisms for the adsorption of iodine from aqueous solutions or from organic solvents on activated carbon were studied. Most adsorption terminated in 24 h, but a very slow adsorption was observed even after 2 d for aqueous solutions. It was found that the adsorbed species could be quantitatively predicted using the Freundlich equation, and that Traube's rule holds for the experimental results of the adsorption equilibria from aqueous solutions and from all organic solutions except alcohols. The intraparticle diffusion coefficients of iodine in organic solvents were determined according to the Boyd equation from the experimental adsorption rate results and correlated to the viscosity of organic solvents.

INTRODUCTION

The separation technique using activated carbon to remove various substances in the liquid phase has been attracting special interest recently. The adsorption method on activated carbon is considered to be very effective for water-soluble organic pollutants. Although it is very important to select suitable activated carbon for use in aqueous solutions, general criteria have not been established for various substances and conditions.

In the present work, the adsorption equilibrium and adsorption rate of iodine from various organic solvents and aqueous iodine–potassium iodide solutions was measured and basic data for the evaluation of activated carbon was obtained.

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EXPERIMENTAL

Materials

Granular activated carbon with a particle size of 20–30 mesh and a BET area of 1000 m^2/g for commercial adsorbent was used after drying at 110°C without further purification. Iodine was dissolved in aqueous potassium iodide solutions, the concentration of which was varied from 0.03 to 0.7 mol/L, and in 10 different organic solvents of GR grade: benzene, cyclohexane, carbon tetrachloride, chloroform, hexane, carbon disulfide, methanol, ethanol, 1-propanol, and 1-butanol.

Analysis

Iodine concentration was determined by titration with sodium thiosulfate using starch as the indicator for aqueous and alcohol solutions, but without any indicators for other organic solutions. The concentration of potassium iodide was calculated from the difference between the iodine concentration and total concentration of iodine and iodide ion, which was measured by titration with potassium iodate solution using carbon tetrachloride as the indicator.

Procedure

Adsorption isotherms were determined as follows. After an activated carbon sample of 0.5 g was added to 50 mL of iodine solution (the concentration of which varied between 1×10^{-3} and 1×10^{-1} mol/dm^3) in a 100-mL stoppered glass flask, it was soaked in a thermostat bath maintained at 30 ± 0.1°C for 48 h. Iodine and iodide ion concentrations in the supernatant were determined after centrifuging. The diffusion coefficient of iodine in a particle of activated carbon from organic solvents was measured by taking out 2 mL samples at about 1 min intervals followed by titration to observe the time variation of its concentration in a solution of 500 mL after introducing a small amount (about 3 g) of activated carbon. The initial iodine concentration in organic solvents was 2×10^{-2} mol/dm^3.

RESULTS AND DISCUSSION

Adsorption Equilibrium

The time to attain equilibrium was determined prior to the experiment on adsorption equilibrium. Figure 1 shows the time variation of the amount of iodine adsorbed. The adsorption rate was extremely rapid immediately after the addition of activated carbon. Although the majority of adsorption seems to be complete in 24 h, very slow adsorption was observed even after 2 d. Such slow adsorption was also observed by Watson et al. (*1*). This very slow adsorption is considered to be due to penetration of the iodine molecules into the carbon structure as suggested by Davis et al. (*2*). The adsoption time was 48 h in the present experiment.

Adsorption isotherms of iodine from aqueous potassium iodide solution at 30°C are shown in Fig. 2 with various potassium iodide concentrations as parameters. The experimental results were plotted according to the Freundlich equation, which is expressed by

$$\log q = (1/n) \log C + \log k \tag{1}$$

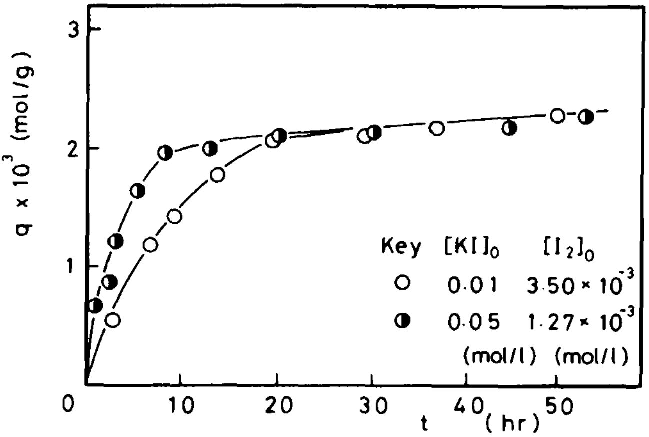

FIG. 1. Relation between amount of iodine adsorbed and adsorption time.

where q = amount adsorbed of iodine per unit mass of activated carbon, mol/g
C = equilibrium concentration of iodine in solution, mol/L
k and n = constants

As is evident from Fig. 2, the amount of iodine adsorbed decreases with the increase of potassium iodide concentration which is attributable to the increase in the solubility of iodine in each potassium iodide solution. An equilibrium (*3*) is expressed by Eq. (2) for the aqueous iodine–potassium iodide mixture which contains iodide and tri-iodide ions and iodine molecules:

$$I_2 + I^- \rightleftarrows I_3^-, \qquad K_A \tag{2}$$

In the case of the adsorption of iodine from an aqueous iodine–potassium iodide mixture on carbon blacks, a time variation of iodide ion concentration was observed which has been ascribed to the adsorption of this ion and the reduction of iodine molecules on carbon black (*4–6*). In activated

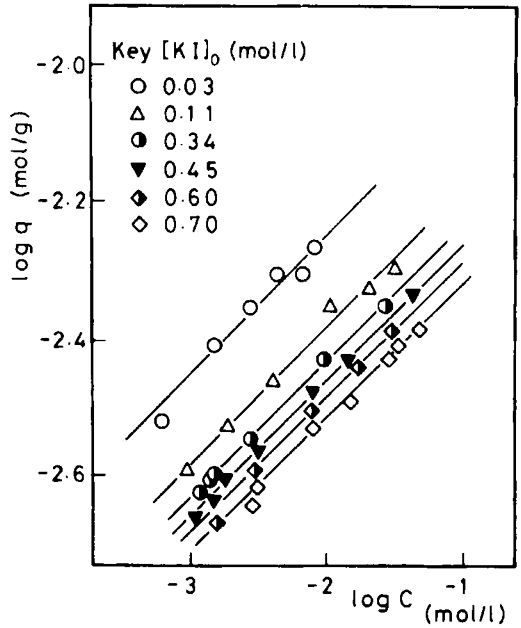

FIG. 2. Adsorption isotherms of iodine on activated carbon from aqueous iodine–potassium iodide solutions at 30°C.

carbon, however, such a time variation of iodide ions has not been observed, and it has been concluded that iodide ions are hardly adsorbed on activated carbon from iodine–potassium iodide solution.

Figure 2 shows that the slopes of the straight lines are nearly constant regardless of the potassium iodide concentration, although the intercept depends on the potassium iodide concentration. Although iodine exists as an iodine molecule, I_2, or as a tri-iodide ion, I_3^-, in aqueous solution, assuming that only one species can be adsorbed on the surface of activated carbon, application of the Freundlich equation to the iodine molecule gives

$$q = k_0[I_2]^{1/n} \tag{3}$$

where k_0 = constant independent of iodine and iodide ion concentrations

The equilibrium concentration of iodine, C, is expressed as

$$C = [I_2] + [I_3^-] \tag{4}$$

Equations (2) to (4) can be combined to give

$$q = k_0 \left(\frac{C}{1 + K_A[I^-]} \right)^{1/n} \tag{5}$$

The logarithm of Eq. (5) gives

$$\log q = \frac{1}{n} \log C + \log k_0 - \frac{1}{n} \log(1 + K_A[I^-]) \tag{6}$$

Combination of Eq. (1) with Eq. (6) gives the relation

$$\log k = f(I^-) = \log k_0 - \frac{1}{n} \log(1 + K_A[I^-]) \tag{7}$$

The intercepts in Fig. 2 which represent log k were plotted against $-\log(1 + K_A[I^-])$ in Fig. 3 according to Eq. (7); the value $K_A = 678$ (*3*) was used. The plotted points in Fig. 3 lie on a straight line of slope $1/n$, the same as the straight lines in Fig. 2, as expected from Eq. (6).

Figures 4 and 5 are the adsorption isotherms of iodine according to Eq. (1) for various kinds of alcohols and for various organic solvents, respectively. The plotted points in these figures appear to lie on straight

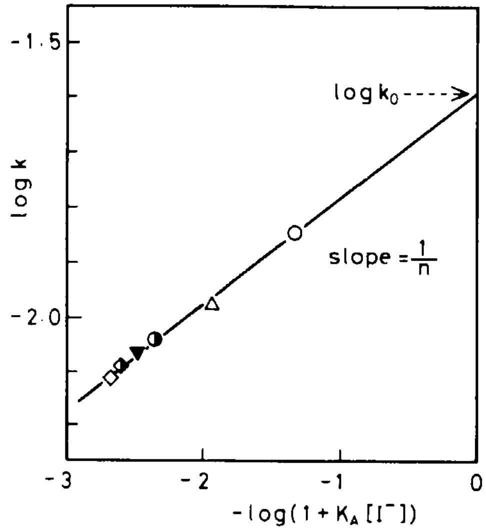

FIG. 3. Variation of log *k* with iodide ion concentration. Keys are the same as those in Fig. 2

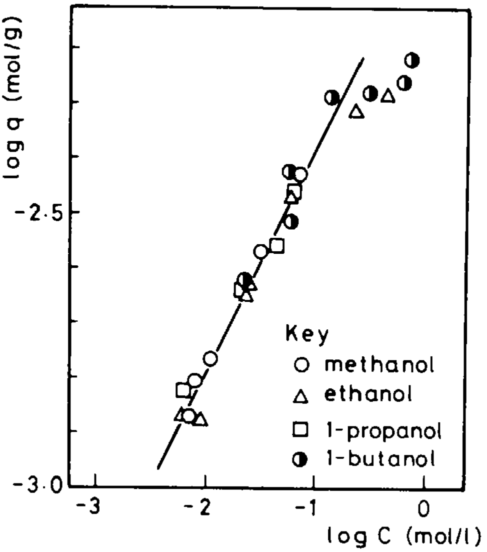

FIG. 4. Adsorption isotherms of iodine on activated carbon from alcohols.

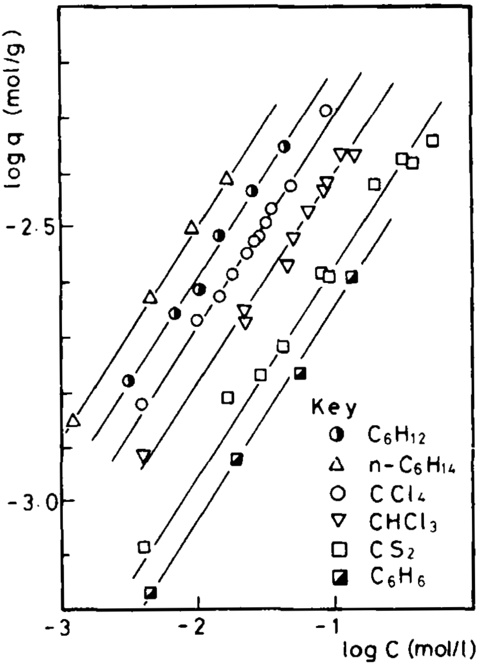

FIG. 5. Adsorption isotherms of iodine on activated carbon from organic solvent excluding alcohols.

lines, which suggests that adsorption from these solvents can also be expressed by the Freundlich equation. The adsorption isotherms of alcohols lie on a single straight line regardless of the number of carbon atoms.

The Freundlich equation for adsorption from saturated solution can be described as

$$\log q_s = \frac{1}{n} \log C_s + \log k \tag{8}$$

Subtraction of Eq. (8) from Eq. (1) gives

$$\log q = \frac{1}{n} \log (C/C_s) + \log q_s \tag{9}$$

where q_s denotes the amount of iodine adsorbed at the saturated concentration of iodine, C_s. Equation (9) suggests that a plot of log q versus log (C/C_s) should give a single straight line regardless of solvent. The experimental results plotted according to Eq. (9) are shown in Figs. 6 and 7 for aqueous potassium iodide solution and for organic solvents systems, respectively, excluding alcohols. As can be seen, all of the plotted points in Figs. 6 and 7 lie on a single straight line regardless of the potassium iodide concentration or the solvent. Therefore, it can be concluded that Traube's rule as expressed by Eq. (9) can be applied to these systems. For alcohol systems, however, Traube's rule cannot be applied because of the high solubility of iodine.

Adsorption Kinetics

When the adsorption rate is controlled by intraparticle diffusion, the extent of adsorption (F), which is defined as the ratio of the iodine uptake at time t (q_t) to that at equilibration (q), is correlated to adsorption time as follows (*7*, *8*):

$$F = \frac{q_t}{q} = \frac{6}{R}\sqrt{\frac{D_i't}{\pi}} \tag{10}$$

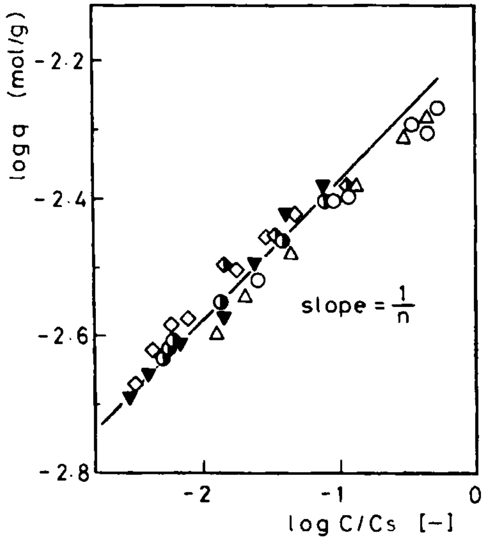

FIG. 6. Adsorption isotherms of iodine from aqueous potassium iodide solution of various concentrations plotted against relative concentration. Keys are the same as those in Fig. 2.

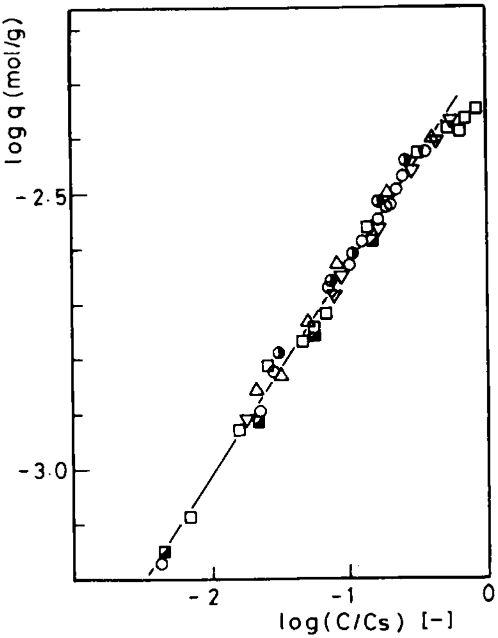

FIG. 7. Adsorption isotherms of iodine from organic solvents excluding alcohols, plotted against relative concentration. Keys are the same as those in Fig. 5.

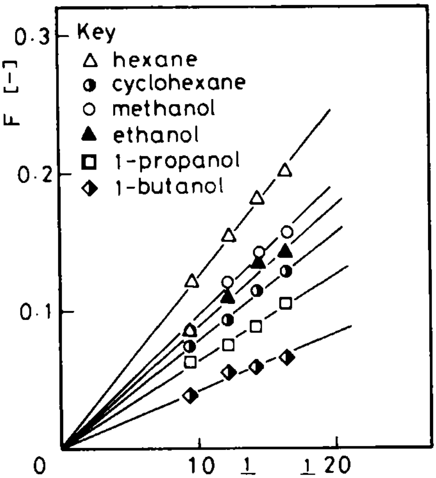

FIG. 8. Adsorption rates of iodine on 20–30 mesh activated carbon from 2×10^{-2} mol/L iodine solution at 30°C.

where R denotes the radius of the adsorbent and D_i' denotes the diffusion coefficient based on the concentration in the solid.

Experimental results of the kinetic measurement are shown in Fig. 8 according to Eq. (10), which indicates the linear relationship between F and $t^{1/2}$ expected from Eq. (10). From the slope of the straight line, the values of D_i' were determined on the basis of Eq. (10) for each solvent and are listed in Table 1. Figure 9 shows the relation between the diffusion coefficient and the reciprocal of the viscosity of each solvent. The adsorption rate of iodine decreases with an increase in the viscosity of the solvent.

Since some interactions between the iodine molecule and each solvent might exist, further investigation of the relationship between the intraparticle diffusion coefficient and the viscosity of a solvent is necessary.

TABLE 1
Relation between Diffusion Coefficient and Viscosity of Solvent

Solvent	Diffusion coefficient D_i' (cm^2/s)	Viscosity η (cP)
Hexane	8.58×10^{-8}	0.29
Methanol	5.14×10^{-8}	0.51
Ethanol	4.42×10^{-8}	1.00
Cyclohexane	3.40×10^{-8}	0.82
1-Propanol	2.22×10^{-8}	1.72
1-Butanol	9.85×10^{-9}	2.28

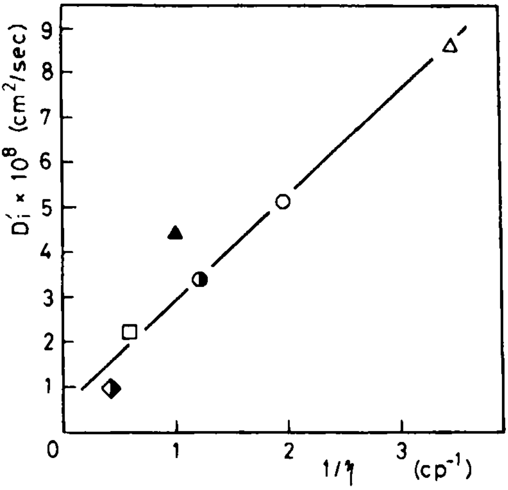

FIG. 9. Relation between diffusion coefficient and reciprocal viscosity of solvent. Keys are the same as those in Fig. 8.

REFERENCES

1. J. W. Watson and Parkinson, *Ind. Eng. Chem.*, *47*, 1053 (1955).
2. O. C. M. Davis, *J. Chem. Soc.*, *91*, 1666 (1907), In *Kasseitan*, J. W. Hassler (translated by T. Oda and Y. Eguchi), Kyoritsu Shuppan, Tokyo, 1966.
3. M. Davies and E. Gwynne, *J. Am. Chem. Soc.*, *74*, 2748 (1952).
4. C. E. Kendall, Dunlop Research Centre, Birmingham, England, Internal Report, C. R. 1103, 1947.
5. W. R. Smith, F. S. Thornhill, and R. I. Bray, *Ind. Eng. Chem.*, *33*, 1303 (1941).
6. M. Mizutori, S. Hagiwara, Y. Fukuda, and K. Kawazoe, *Nippon Gomu Kyokaishi, 35*, 507 578 (1960).
7. G. E. Boyd, L. L. Myers, and A. N. Adamson, *J. Am. Chem. Soc.*, *69*, 2836 (1947).
8. K. Urano and R. Kiyoura, *Kogyo Kagaku Zasshi, 73*, 1921 (1970).

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