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Abstract

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MECHANISM OF IODINE TRANSFER UNDER INTRADIFFUSIONAL KINETICS OF ITS ADSORPTION ON CHARCOALS FROM DIFFERENT SOLVENTS

(Presented by Academician M. M. Dubinin on October 8, 1960)

Unlike gases (¹), the mechanism of transfer of dissolved substances in porous sorbents has scarcely been studied.

We studied the transfer of molecular iodine under intradiffusional kinetics of its adsorption from different solvents on different charcoals. The solvents were dehydrated and distilled C₂H₅OH, C₆H₆, and CCl₄, as well as distilled water. The adsorbents were BAU, KAD, and AG charcoals.

Table 1

Charcoals	BAU	KAD	AG	Charcoals	BAU	KAD	AG
Gravimetric weight Δ , g/cm ³	0.21	0.35	0.52	Pore volume = $1/\delta - 1/\rho$, cm ³ /g	2.30	1.01	0.63
Apparent weight δ , g/cm ³	0.35	0.64	0.88	Porosity = $(\rho - \delta)/\rho$	0.805	0.65	0.55

Charcoals	BAU	KAD	AG	Charcoals	BAU	KAD	AG
True specific weight ρ , g/cm ³	1.80	1.82	1.98	Micropore volume*, in cm ³ /g	0.180	0.193	0.196
Volume of one gram of charcoal $1/\delta$, cm ³ /g	2.85	1.56	1.14	in percent	7.8	19.1	31.8
				Ash, %	0.2	10.3	6.3
				Moisture, %	0.67	1.87	3.80

* This volume was calculated from the relation: $126.9 a_{\max}/4.93 \cdot 1000$, where a_{\max} was calculated from the iodine adsorption isotherms from water (see Table 2) at the equilibrium concentration $y = 2.3$ mg-eq/L, equal to the solubility of iodine in water at 20° (see Table 3).

The BAU and AG charcoals were washed with hydrochloric acid, and AG was additionally oxidized with iodine. Then they were washed with water and ignited in a muffle furnace at 800–850° until 10% burn-off for BAU and 40% for AG (until the complete disappearance of HCl and J₂ in the exit gases). KAD was not subjected to treatment. All charcoals were sieved and dried at 100°. The work was carried out with fractions having an average grain diameter of 0.25 cm.

Table 2

During iodine adsorption	On BAU	On BAU	On KAD	On KAD	On AG	On AG
	z	y_1	z	y_1	z	y_1
From H ₂ O	7.31	0.063	8.05	0.21	10.12	0.75
From C ₂ H ₅ OH	1.13	0.22	1.00	0.23	0.95	0.52

During iodine adsorption	On BAU	On BAU	On KAD	On KAD	On AG	On AG
From C_6H_6	1.54	0.42	1.22	0.30	0.93	0.30
From CCl_4	2.85	0.23	1.61	0.38	1.60	0.69

The statics of iodine adsorption was studied by previously described methods^(2,3) at a temperature of 18-23°. The results of equilibrium adsorption (according to iodine analyses on the BAU and AG charcoals) are presented in Fig. 1. If the adsorption isotherms obtained on KAD charcoal were plotted on the same Fig. 1, they would lie between the corresponding isotherms obtained on BAU and AG charcoals. Table 2 gives the constants (z and y_1) of the Langmuir equations $a = zy/(y_1 + y)$, found from the experimental points by the method of least squares (z in mg-eq/g; y_1 in mg-eq/L).

Table 3 gives the values of the static adsorption of iodine a_0 from all solvents at the equilibrium concentration $C_0 = 1$ mg-eq/L, chosen for carrying out the kinetic experiments, which were also performed at

Table 3

Diffusion of iodine in charcoal grains

Charcoal	Medium	Heat of wetting at 20°, cal/g	Equilibrium adsorption		Half-saturation time $t_{1/2}$, min	$\Gamma = \frac{a_0 \delta}{C_0}$	$\frac{D_\ell \varepsilon}{\Gamma}, \text{ cm}^2/\text{sec} \cdot 10^7$	$\frac{D_a \Gamma}{D_\ell \varepsilon}$	$D_a, \text{ cm}^2/\text{sec} \cdot 10^7$
			a_0 , mg-equiv/g	$D_{\text{eff}}, \text{ cm}^2/\text{sec} \cdot 10^7$					
BAU	H_2O	7.3	6.88	0.265	300	2750	0.038	5.0	0.227
BAU	C_2H_5OH	18.0	0.93	0.245	325	371	0.24	—	—
BAU	C_6H_6	19.8	1.09	0.271	294	436	0.36	—	—
BAU	CCl_4	12.6	2.32	0.083	960	930	0.12	—	—
KAD	H_2O	11.2	6.65	0.230	346	4250	0.020	9.5	0.210
KAD	C_2H_5OH	19.2	0.81	0.072	1100	519	0.14	—	—
KAD	C_6H_6	19.2	0.94	0.083	960	602	0.21	—	—
KAD	CCl_4	16.7	1.17	0.083	960	750	0.12	—	—
AG	H_2O	12.3	5.78	0.210	380	5090	0.014	12.9	0.196
AG	C_2H_5OH	19.8	0.62	0.040	1980	547	0.11	—	—
AG	C_6H_6	22.8	0.72	0.066	1200	633	0.17	—	—

Figure 1

Figure 1: Figure 1

Charcoal	Medium	Heat of wetting at 20°, cal/g	Equilibrium ad-sorption		Half-saturation time $t_{1/2}$, min	$\Gamma = \frac{a_0 \delta}{C_0}$	$\frac{D_\ell \varepsilon}{\Gamma} \cdot 10^7$, cm ² /sec	$\frac{D_a \Gamma}{D_\ell \varepsilon}$	$\frac{D_a}{\Gamma} \cdot 10^7$, cm ² /sec
			a_0 , mg-equiv/g	D_{eff} , cm ² /sec · 10 ⁷					
AG	CCl ₄	19.7	0.95	0.080	1000	830	0.09	—	—

Diffusion coefficient of iodine at 20°, $D_\ell \cdot 10^5$: in H₂O, ~1.3; C₂H₅OH, ~1.1; C₆H₆, 1.95; CCl₄, 1.36.

Solubility of iodine at 20° in mg-equiv/l: in H₂O, 2.3; C₂H₅OH, 1698.2; C₆H₆, 946.0; CCl₄, 190.4.

18-23°. Samples of charcoals (0.1 g in water and 0.4 g in other solvents), boiled in the corresponding solvent, were transferred into bottles with ground-glass stoppers of 2.5 l capacity and were filled with 1.5 l of iodine solution at a concentration of 1 mg-equiv/l. The bottles were fixed in a box that could rotate about a horizontal axis by means of a motor with a reduction gear. In this way optimum conditions for supplying iodine to the charcoal grains were achieved, and the saturation regime could be regarded as intradiffusional. Our experiments were carried out at 60 rev/min. To maintain the initial iodine concentration, after definite time intervals the liquid above the charcoal was replaced by a fresh portion of the initial iodine solution. After a definite time had elapsed, the charcoal was transferred into a mortar, and the adsorbed iodine in it was determined as described earlier (2, 3). The deviations of the determinations from the means were about ±5%.

Fig. 1. Static adsorption of iodine on BAU charcoal (dashed lines) and on AG charcoal (solid lines). *I*—from H₂O, *II*—from C₂H₅OH, *III*—from C₆H₆, *IV*—from CCl₄.

The mean results for the saturation (a) of BAU and AG charcoals with time are given in Fig. 2, and the relative saturations a/a_0 of all charcoals in Fig. 3. From these curves the half-saturation times (t), corresponding to $a/a_0 = 0.5$, were found, and from them, by the method of successive approximations, the effective coefficients of internal diffusion (D_{eff}) were calculated from the equation

$$a/a_0 = 1 - \frac{6}{\pi^2} \sum_{n=1}^{n=\infty} \frac{1}{n^2} \cdot e^{-\frac{n^2 \pi^2 D_{\text{eff}} t}{R^2}}, \quad (1)$$

Fig. 2. Kinetics of iodine adsorption on BAU and AG carbons (designations the same as in Fig. 1)

Figure 2: Fig. 2. Kinetics of iodine adsorption on BAU and AG carbons (designations the same as in Fig. 1)

Fig. 3. Kinetics of relative saturation of carbons with iodine: for BAU (a), for KAD (b), and for AG (v) (designations the same as in Fig. 1)

Figure 3: Fig. 3. Kinetics of relative saturation of carbons with iodine: for BAU (a), for KAD (b), and for AG (v) (designations the same as in Fig. 1)

with not fewer than 4 terms of the series being taken (see Table 3). Table 3 gives the heats of wetting of the charcoals by solvents, which were determined in small Dewar vessels with the aid of a bead thermistor of type T8S2, with deviations from the mean value of the order of 0.3–0.4 cal/g.

As can be seen, the heats of wetting of the carbons by each liquid increase from BAU to AG. The heats of wetting by water are smaller than by nonaqueous liquids. From BAU to AG the volume of micropores accessible to iodine increases, while the total porosity sharply decreases (Table 1). The values of a_0 decrease

Fig. 2. Kinetics of iodine adsorption on BAU and AG carbons (designations the same as in Fig. 1)

from BAU to AG in the direction opposite to the change in the heats of wetting. On each carbon, a_0 decreases along the series of solvents: H_2O , CCl_4 , C_6H_6 , C_2H_5OH (see also Fig. 1), in accordance with the rule that adsorption decreases with increasing solubility of the substance in the given solvent (Table 3). The curves $a = f(t)$ for each carbon pass one above another, also in accordance with the statics of adsorption (Fig. 2), while the curves of relative saturation $a/a_0 = f(t)$ (Fig. 3) have features associated with the porosity of the carbons.

If, following Damköhler⁽⁴⁾, it is assumed that the transfer of iodine in the grains along the pore walls proceeds with diffusion coefficient D_a , and in the volume of the pores, in the liquid filling the pores, with coefficient D_p , then for $\Gamma \gg 1$ one may write:

$$D_{\text{eff}} = \frac{D_p}{\Gamma} + D_a = \frac{D_p}{\Gamma} \left(1 + \frac{D_a \Gamma}{D_p} \right). \quad (2)$$

Fig. 3. Kinetics of relative saturation of carbons with iodine: for BAU (a), for KAD (b), and for AG (v) (designations the same as in Fig. 1)

The ratio $\frac{D_a \Gamma}{D_p}$ is a criterion for the participation of substance transfer along the pore walls relative to transfer in the pore volume⁽¹⁾. Assuming that diffusion

in the volume, at least in macropores, proceeds as in a free liquid, where the diffusion coefficient is D_1 , one may write

$$D_p = D_1 \varepsilon, \quad (3)$$

where ε is the effective porosity of the grains filled with liquid; Γ is the adsorption coefficient, which in our experiments characterizes the capacity of 1 ml of carbon grains, in contrast to the usual characteristic of the capacity of the adsorbent in 1 ml of a column with charge. In our experiments $\Gamma = a_0 \delta / C_0$ (4), where δ is the apparent specific gravity of the carbon. Using (2) and (3), we write:

$$D_{\text{eff}} = \frac{D_\ell \varepsilon}{\Gamma} \left(1 + \frac{D_a \Gamma}{D_\ell \varepsilon} \right). \quad (5)$$

Assuming that, in the adsorption of iodine from water, the effective porosity of the carbons will differ little from that calculated from the specific gravities, we found, using the values of ε from Table 1, the values: $\frac{D_\ell \varepsilon}{\Gamma}$, $\frac{D_a \Gamma}{D_\ell \varepsilon}$, and D_a (Table 3).

In the adsorption of iodine from water, $\frac{D_\ell \varepsilon}{\Gamma}$ is always considerably smaller than D_{eff} , while D_a values are large and decrease somewhat from BAU to AG. The surface-transfer criterion $\frac{D_a \Gamma}{D_\ell \varepsilon}$ increases strongly from BAU to AG, because with decreasing porosity of the carbons the value $\frac{D_\ell \varepsilon}{\Gamma}$ decreases by almost a factor of 3.

In adsorption from nonaqueous media, on the contrary, D_{eff} proved to be smaller than $\frac{D_\ell \varepsilon}{\Gamma}$. Evidently, the molecules of these liquids, being adsorbed themselves, form adsorption layers of different thicknesses, as a result of which transfer is hindered not only along the pore walls (D_a is close to 0), but diffusion through the pore volume is also slowed because of the "decrease in the free openings of the pores." It is possible that this slowing is affected by the need to displace liquids from the pores during the diffusion of iodine into them. If one takes $D_a \simeq 0$ in experiments with benzene, then, by setting $\frac{D_\ell \varepsilon'}{\Gamma} \simeq D_{\text{eff}}$, one can find the effective porosity of the carbons ε' . For BAU, KAD, and AG it was found to be: 0.60; 0.26; 0.20, and the ratio $\frac{\varepsilon}{\varepsilon'}$ was 1.34; 2.50, and 2.75, i.e., for the less porous carbons the influence of C_6H_6 on the "decrease in pore openings" naturally proved to be greater.

Because of the basically different mechanism of iodine transfer in the pores of carbons during adsorption from water and from nonaqueous liquids, the influence of carbon porosity is manifested very differently. In adsorption from water,

D_{eff} depends little on porosity, since transfer proceeds mainly along the pore walls, and D_a , as it turned out, depends little on the type of carbon. In adsorption from C_6H_6 (and from alcohol), D_{eff} depends strongly on the type of carbon, since in these cases the principal type of transfer is diffusion through the pore volume, determined by the value $\frac{D_\ell \varepsilon'}{\Gamma}$, which can vary severalfold from one carbon to another. Apparently, in the adsorption of iodine from CCl_4 , surface transfer does not entirely lose its importance, as in the case of adsorption from C_6H_6 and from C_2H_5OH , owing to which the differences in D_{eff} for different carbons proved to be smoothed out.

In the intradiffusion transfer of iodine during its adsorption from water on carbons, the principal type is surface transfer (along the pore walls). This mechanism loses its importance in the adsorption of iodine from nonaqueous media (CCl_4 , C_2H_5OH , and C_6H_6), especially from benzene and alcohol. In these cases diffusion of iodine through the pore volume predominates, as a result of which the effective diffusion coefficients may vary greatly for different carbons, depending on their effective porosity and adsorption capacity.

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