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Abstract

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KINETICS OF THE PHYSICAL ADSORPTION OF ETHYLENE FROM MIXTURES

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Recently, processes whose rate is determined by diffusion inside granules have been acquiring ever greater importance. However, the field of intradiffusion kinetics has been insufficiently developed, both theoretically and experimentally. Only in the last two years have papers on the intradiffusion kinetics of the adsorption of a single substance begun to appear systematically ([1–3]).* In particular, the literature contains no data whatsoever on the rate of uptake of ethylene from a stream of gas mixtures, despite the fact that such data are very important for the development of adsorption methods for the separation and analysis of hydrocarbon gases.

In the present work the rate of adsorption of ethylene from mixtures with H_2, N_2, and CH_4 on industrial activated carbon of grade AG-2 was studied. The choice of systems is connected with the development of a technology for isolating ethylene from gas mixtures with a low content of the target component; however, the method developed and the results of the investigation have more general significance.

For carrying out the investigation, a differential method for measuring the kinetics of adsorption of mixtures was specially developed,** since the methods used previously do not make it possible to obtain data convenient for treatment, owing to the dependence of the coefficient of internal diffusion on the composition of the adsorbate. The principle of this method is that a mixture of specified composition is passed through an adsorption cell with a thin layer of adsorbent until equilibrium is established. Then, for a precisely fixed time, a second mixture of different but similar composition is passed through the cell. The change in the amount of adsorption of the components is calculated from the data of chemical analysis of the mixture desorbed from the carbon. Desorption is carried out by evacuation with a Töpler pump of the adsorbent heated to 200°. Such an experimental procedure corresponds to a small change in the coefficient of internal diffusion during adsorption and to an almost linear relationship between changes in the adsorption value a and the concentration c in the gas phase.

The value of the degree of conversion of the grain is calculated by the formula

Figure 1

Figure 1: Figure 1

$$F = \frac{a - a_\infty}{a_\infty - a_0}, \tag{1}$$

where a_0 and a_∞ are the amounts of adsorption of ethylene, in equilibrium with the mixtures of the concentration interval under investigation; a is the amount of adsorption of ethylene at the given time of contact with the mixture having the higher ethylene content.

* These articles give references to earlier work.
** This method was developed in 1953, before the publication of Karman' s paper ([1]), which describes a method for measuring the kinetics of adsorption of a single substance based on an analogous principle.

For measuring the kinetics of adsorption of mixtures, a special apparatus was constructed with a small dead volume of the adsorption cell, ensuring identical conditions of flow around the grains of short and long adsorbent beds. The main part of the apparatus—the adsorption cell—consists of two stopcocks with wide bores, connected by a section of glass tubing no more than 1.5 cm long. This tube and the bore of the stopcock have almost the same internal diameter, equal to 1.4 cm. Perpendicular to the main bore in each stopcock there is a one-sided passage of small diameter for evacuating the mixture from the main bores when the stopcocks are closed. The adsorbent is placed in the tube of the cell between two screens and beds of grains of inert packing, identical in shape and size to the adsorbent granules. There is an electrical winding on the cell tube. The use of a special lubricant made of lithium stearate and high-boiling fractions of aviation oil, as well as the passage of cold water through the stopcock plugs, makes it possible to avoid its softening during heating and the lubricant getting onto the adsorbent. The mixtures used in the work were prepared from gases purified with charcoal and subjected to double recondensation. The values of the narrow adsorption intervals Δa and ethylene concentration Δc, in which the measurements were carried out, varied from 0.7 to 4.5 normal cm^3/g and from 0.1 to 6.4% C_2H_4, respectively.

Fig. 1. a–C_2H_4—H_2; b–C_2H_4—CH_4; v–C_2H_4—N_2; curve–theoretical data

For processing the experimental data, the usual equation of intradiffusion adsorption kinetics for one substance with a constant coefficient is used. The possibility of applying this equation follows from the entire set of data obtained in the present work. Namely, it was found that: 1) the rate of ethylene uptake does not depend on the rate of the gas flow (the rate was varied twofold from 1.85 to 3.70 $l/min \cdot cm^2$); 2) in the initial stage of the adsorption process there is a linear dependence of the degree of exhaustion of the grain on the square

Fig. 2

Figure 2: Fig. 2

root of the contact time of the gas mixture with the adsorbent; 3) the adsorption and desorption rate curves coincide, which indicates practical constancy of the diffusion coefficients within the investigated interval; 4) the presence of the second component practically does not reduce the adsorption of ethylene, and the amount of the second component displaced by ethylene is insignificant in comparison with the magnitude of ethylene adsorption.

The calculation of the internal diffusion coefficients D was carried out from the dimensionless theoretical curve giving the degree of exhaustion of the grain F as a function of the Fourier criterion $\mathrm{Fo} = Dt/R^2$, calculated by us for the case of diffusion into cylindrical granules of radius R and length $2l$, at a specified value of the shape simplex $s = R/l$, equal to 0.308. Deviations of the experimental values of D, corresponding to different contact times, from the mean values have no systematic character and do not exceed the possible measurement errors (10%). Then, from the mean values of D, the values of the Fourier criterion were calculated for different fillings of the adsorption volume. Fig. 1 shows that the experimental data for all systems satisfactorily lie on the theoretical dimensionless curve F–Fo. The magni-

the Biot criterion values $\mathrm{Bi} = \beta' R/D$, calculated from experimental data, for all the systems investigated lie within the range from 60 to 190. All this confirms the intradiffusional character of the kinetics of ethylene adsorption from the mixtures studied and the applicability, for describing the experimental data, of the simple equation of internal diffusion with a constant coefficient.

The data obtained in this work on the dependence of the internal diffusion coefficient on the magnitude of ethylene adsorption, on the nature of the second component, on the porosity of the sorbent, and on temperature are presented in Fig. 2.

In all the systems investigated, the values of the internal diffusion coefficients increase sharply with increasing amount of adsorbed ethylene.

Fig. 2. a –C_2H_4—H_2; b –C_2H_4—N_2; v –C_2H_4—CH_4; g –C_2H_4—Ar at 25°; d and e –C_2H_4—CH_4 system: d –at 50°, e –at 75°; zh and z –C_2H_4—N_2 system at 25°: zh –charcoal A, z –charcoal B.

ethylene. For the nitrogen–ethylene and methane–ethylene systems a linear dependence is observed over the entire range of adsorption values; for the hydrogen–ethylene system the linear character of the dependence is retained if the curve is divided into two sections.

A strong dependence of the internal diffusion coefficient on composition may occur for any type of transport of a substance inside granules. Indeed, in surface diffusion

$$D = D^0 \exp(-\alpha A/RT),$$

where D^0 is the pre-exponential factor; α is a constant coefficient; A is the adsorption potential, which depends strongly on the magnitude of adsorption. When the substance moves in the pore volume,

$$D = \overline{D}/\Gamma,$$

where $\overline{D}$ is the coefficient of volume or molecular diffusion; $\Gamma = \partial a/\partial c$ is a variable parameter, usually strongly dependent on the magnitude of adsorption. In addition, in the case of molecular diffusion $\overline{D}$ also depends on the degree of surface filling, since different adsorption values correspond to pores of different sizes. It follows from this that only when volume diffusion plays the determining role can the product $D\Gamma$ be independent of the magnitude of adsorption. Calculation shows that, in the region studied, $D\Gamma$ decreases with surface filling by 35-40%. Thus, although $D\Gamma$ is not constant, it changes considerably more slowly than D. This indicates that, in the process of ethylene transport inside charcoal granules, along with volume diffusion, molecular and/or surface diffusion is of substantial importance.

The activation energies of the diffusion process, calculated from the experimental data in the temperature intervals 25—50° and 25—75° at adsorption values of 5.10 and 6.78 normal cm^3/g, are 5100 and 5500 cal/mole, respectively.

respectively, whereas the heats of adsorption are 5600 and 5200 cal/mole. The closeness of these values indicates the significant role of volume and (or) molecular diffusion in the process of ethylene transport inside the adsorbent. The substantial role of volume and (or) molecular diffusion in this process is also indicated by the weak dependence of the product $D\Gamma$ on temperature. Indeed, in the intervals from 25 to 75° and from 25 to 50°, the product $D\Gamma$ changes only from $0.78 \cdot 10^{-2}$ to $0.67 \cdot 10^{-2}$ cm^2/sec.

It has been found that the value of the internal-diffusion coefficient depends substantially on porosity. In samples of AG-2 carbons with bulk densities 0.675 (A) and 0.540 (B), differing from one another in total pore volume by 30% and in the volumes of macro-, micro-, and transitional pores by 22, 44, and 34%, the diffusion coefficients are, respectively, $3.70 \cdot 10^{-5}$ and $8.9 \cdot 10^{-5}$ cm^2/sec. This difference in the values of the internal-diffusion coefficients cannot be explained by a change in the coefficient Γ, since the product $D\Gamma$ also changes from $0.46 \cdot 10^{-2}$ to $1.37 \cdot 10^{-2}$ cm^2/sec. Such a strong dependence on porosity may occur if the main role in the transport of substance inside the grain is played by molecular diffusion.

The influence of the second component on the value of the internal-diffusion coefficient is clearly manifested over almost the entire investigated range of ethylene adsorption values. Only at low fillings of the adsorption volume (2.5 $n.cm^3/g$)

do the values of the internal-diffusion coefficients not differ substantially from one another. But even in the region of medium surface fillings (12.6 n.cm^3/g), the ratio of D in the system with H_2 to D in the systems with N_2, CH_4, and Ar is, respectively, 1.5; 1.6; and 3.5, whereas the ratio of the volume diffusion coefficients for these systems is, respectively, 2.8; 3.7; and 4.5. This shows that volume diffusion, along with one or two other types of transport, plays a substantial role in the process of ethylene transport.

From the foregoing it follows that, within the framework of the usual concepts of the process of ethylene transport inside a grain, there is a superposition of three types of transport: volume, molecular, and surface diffusion, the last of which plays a secondary role. It should be noted, however, that the process of ethylene transport inside granules cannot be completely described solely on the basis of the usual concepts of volume and molecular diffusion, since analysis of the absolute values of the experimental coefficients of internal diffusion ($\sim 10^{-4}$ -10^{-5} cm^2/sec) and of the products $D\Gamma$ ($\sim 5 \cdot 10^{-3}$–10^{-2} cm^2/sec) leads either to implausibly small values of the effective cross section and of the tortuosity coefficient (if volume diffusion is assumed), or to values of the pore radius comparable with molecular dimensions—of the order of ten angstroms (in the case of molecular diffusion).

From the internal-diffusion character of the adsorption kinetics established in this work there follow a number of important practical conclusions concerning the influence of individual parameters on the separation process in a moving and stationary bed, as well as concerning the requirements imposed on the adsorbent. The numerical characteristics obtained in the work make it possible to calculate the dynamics of ethylene adsorption.

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Note: Figure translations are in progress. See original paper for figures.