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The Surface Flow of Adsorbed Carbon Dioxide on Active Carbon

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The surface flow of carbon dioxide adsorbed on active carbon has been measured with the use of Carman's steady flow method at temperatures of −21°, −9°, 0°, and +25°C. The supplementary measurements of adsorption isotherms at the same temperatures have been performed in the standard volumetric apparatus. The results obtained are interpreted in terms of surface diffusion and surface viscous flow.

1. INTRODUCTION

The surface flow of physically adsorbed gases in microporous media has drawn considerable attention during recent years (*1–4*). This process has been frequently described (*1, 2, 3*) as a two-dimensional diffusion governed by Fick's law:

$$\mathbf{J}_s = -D_s \nabla_r \rho_s \qquad (1)$$

where $\mathbf{J}_s = \rho_s \mathbf{v}$, ρ_s, surface density of adsorbed gas; $\mathbf{v}$ is the two-dimensional velocity of adsorbed molecules; D_s, the diffusion coefficient for adsorbed gas; and ∇_r, the nabla operator acting on the coordinates. On the other hand it has been pointed out (*5, 6, 7*), that the surface steady flow of adsorbed gas has to be regarded as a two-dimensional viscous flow described by equation

$$\nabla_r \pi' + L_{vv} \mathbf{v} = 0 \qquad (2)$$

where π' is the surface pressure of adsorbed gas; and L_{vv}, the phenomenological coefficient describing the momentum transfer between adsorbed gas and underlying solid.

Equation (2) has been derived by using the thermodynamics of irreversible processes (*8, 9, 10*) and confirmed by statistical mechanical considerations (*11*).

The purpose of this paper is the direct comparison of the above-mentioned descriptions of the surface flow in the case of carbon dioxide adsorbed on active carbon. We essentially adapt the steady state method of the measurements of surface flow of adsorbed gas as described by Carman and Malherbe (*12*). This method and measurements of adsorption isotherms make it possible to calculate and compare the quantities $K = k_s D_s$, $\alpha = k_s / L_{vv}$ (where k_s is the tortuosity factor, constant for a given microporous medium) for the investigated system.

2. EXPERIMENTAL

The measurements of surface flow of carbon dioxide have been performed using a steady flow apparatus similar to that described by Carman (*13*). The plug of microporous medium was formed by compression of active carbon in the device shown in Fig. 1.

Active carbon was compressed between two small porous plugs formed from the compressed copper wire. After the formation of the carbon microporous plug two holders were introduced to a steel matrix, as indicated in Fig. 2.

The aim of the copper plugs and steel holders is to eliminate the swelling of carbon plugs during the flow measurements. The resistance of copper plugs to the flow of the gas is negligibly small as compared to the resistance of carbon microporous plugs and can not be considered in the description of the surface flow process. The matrix with the carbon plug was connected with the steady flow apparatus exactly as indicated in Carman's paper (*13*). The contribution of the volume flow to the total flow of carbon

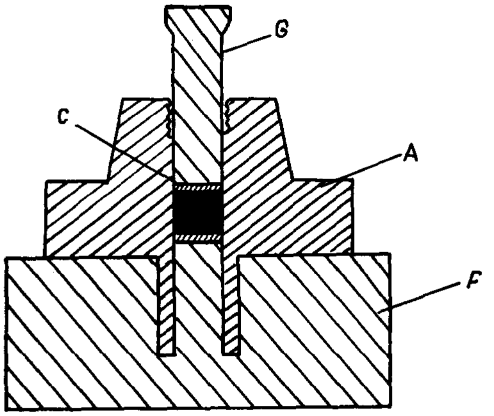

FIG. 1. Compression apparatus: A, matrix; F. support; G, piston (all parts made from hardened steel); C, microporous plug.

dioxide across the carbon microporous plug was eliminated by separate measurements of the flow of nitrogen. It has been assumed that the adsorption and surface flow of nitrogen is not significant under the experimental conditions, because the possible concentration gradient of adsorbed nitrogen along the carbon plug should be negligibly small as compared to the gradients of adsorbed carbon dioxide. This assumption has been strongly confirmed by the pressure dependence of the permeability of nitrogen obtained from experiments. It appears that this permeability does not depend on the pressure of nitrogen—exactly what should be expected for the volume Knudsen flow.

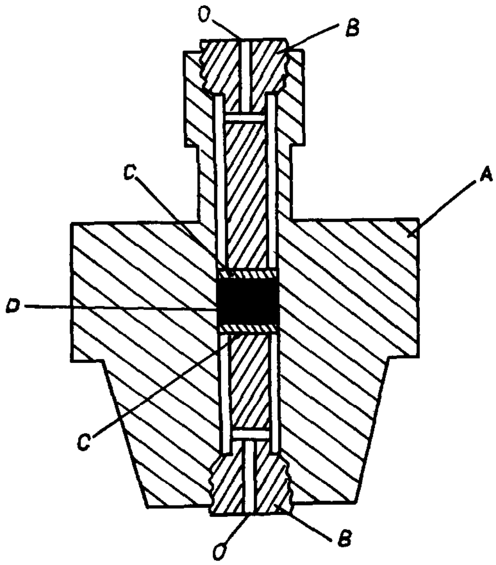

FIG. 2. Microporous plug with holders added: A, matrix; B, holders; C, copper plugs; D, carbon plug.

The volume flow measurements were performed at temperatures of −21°, −9°, 0°, and +25°C. These were achieved by surrounding the matrix with carbon plug by constant temperature baths. As the temperature bath a large Dewar vessel was used. Temperatures of 0°, −9°, and −21°C were obtained using a melting ice–water mixture; potassium chloride–water eutectic; and sodium chloride–water eutectic, respectively. The temperature of +25°C was obtained with the use of a conventional thermostat. Temperature control of ±0.5°C was maintained in all cases.

The measurements of adsorption isotherms at +25°, 0°, −9°, and −21°C were performed in a conventional volumetric apparatus with the use of the standard technique.

The active carbon investigated was prepared in the laboratory of the Central Institute of Mines in Katowice. It has a specific surface of 560 m^2/g and a density of 2.50 g/cm^3. The relatively high density is due to metallic impurities, largely of magnesium and calcium (about 1 wt %). The Commercial carbon dioxide was used as adsorbate; water was removed by the use of dry calcium chloride and phosphorus pentoxide. As the reference gas commercial nitrogen was used; oxygen was removed by flow through copper chips heated to 400°C and activated by hydrogen.

3. RESULTS

The results of measurements of adsorption isotherms at +25°, 0°, −9°, and −21°C have been gathered in Table 1 and presented in Fig. 3. On the basis of the adsorption isotherms and the surface flow measurements the coefficients K and α have been calculated. The surface flow data are presented in Table 2. In the second column of this table the total flow of carbon dioxide $B = WL/\Delta pA$ is given, where W is the total flow in mmole/sec; L, the length of the carbon plug (in cm); Δp, the difference

TABLE 1
ADSORPTION ISOTHERM DATA

Temperature (°C)	Pressure (mm Hg)	Amount of the adsorbed gas [ml(STP)/g]
−21°	107	22.6
	128	24.4
	185	31.7
	220	30.1
	295	42.9
	351	49.4
	421	55.3
	509	62.7
−9°	98	11.6
	115	16.5
	203	24.1
	261	29.4
	331	34.3
	428	41.7
	493	46.1
0°	127	13.0
	168	16.2
	191	18.0
	230	19.6
	276	22.3
	323	25.7
	390	28.4
	501	33.8
+25°	114	5.2
	129	5.5
	210	7.8
	237	8.8
	362	12.2
	409	13.7
	577	16.4

of the gas pressure on both sides of the carbon plug, in dyne/cm^2; and A, the cross section of the plug, in cm^2. In the third column the surface flow B_p is presented; it has been calculated by eliminating from the total carbon dioxide flow the volume flow contribution—the method described in detail in Ref. (*12*). The dependence of coefficients K and α on the coverage of the adsorbent surface by adsorbate in cm^3 (STP)/g is illustrated by diagrams in Figs. 4 and 5.

4. DISCUSSION

The dependence of coefficients K and α on the concentration of the adsorbate on the surface, presented in Figs. 4 and 5, is the most essential point of our investigation. As the pore structure of the carbon plug was the same in all experiments, the tortuosity factor k_s can be regarded as a constant characterizing the microporous medium, and the concentration dependence of K and α correspond essentially to the concentration dependence of diffusion coefficient D_s and phenomenological coefficient L_{vv}. Figure 4 clearly shows a strong concentration dependence of coefficient D_s. This dependence is larger for higher temperatures and what follows—lower surface coverages by adsorbate. On the other hand Fig. 5 indicates that for temperatures 0°, −9°, and −21°C the concentration dependence of phenomenological coefficient L_{vv} is much smaller. For −21°C coefficient L_{vv} is constant over the wide range of surface coverages. Unfortunately the calculations of L_{vv} for +25°C have not given consistent values because of a particularly strong influence of the experimental error in this region.

Let us examine in more detail the relative independence of the phenomenological coefficient L_{vv} of the surface concentration of carbon dioxide, demonstrated by experiments. The phenomenological coefficient has an exact physical interpretation given by the law of momentum conservation for an adsorbed layer (*8–10*)

$$\rho_s(d\mathbf{v}/dt) = -\nabla_{\mathbf{r}}\pi' - L_{vv}\mathbf{v} \qquad (3)$$

where t is time. This coefficient characterizes the resistance to the motion of the unit of surface of the adsorbed layer. Thus the relative independence of L_{vv} of the surface concentration leads to the rather unexpected conclusion that this resistance does not depend on the amount of gas adsorbed on the unit of the surface. It should be rather expected that the resistance mentioned above is larger the more molecules of adsorbed gas are present on the surface and so the coefficient L_{vv} should be an increasing function of the surface concentration. Statistical mechanical considerations (*11*) indeed lead to the conclusion that, for diluted adsorbed layers on the uniform surfaces described adequately as a two-dimensional ideal gas, L_{vv} is a linear function of ρ_s, namely $L_{vv} = \rho_s\beta$, where β is the friction

TABLE 2

SURFACE FLOW DATA FOR ACTIVE CARBON, SPECIFIC SURFACE $S_0 = 560\ \mathrm{m^2/g}$, POROSITY, 0.6, WITH A FLOW OF CO_2

Pressure $p = \frac{1}{2}(p_1 + p_2)$ (mm Hg)	Total flow $B \times 10^{10}$ (mmole sec/g)	Surface flow $B_p \times 10^{10}$	$K \times 10^4$ (cm²/sec)	$\alpha \times 10^6$ (sec cm²/g)
		Temperature, −21°C		
276	3.26	1.08	3.29	3.25
331	3.56	1.39	4.23	3.64
393	3.78	1.60	4.88	3.70
456	3.98	1.80	5.49	3.72
523	4.36	2.18	6.64	4.05
		Temperature, −9°C		
294	3.36	1.24	5.02	6.11
354	3.34	1.22	4.91	5.25
397	3.41	1.29	5.21	5.09
437	3.63	1.51	6.19	5.56
509	4.03	1.91	7.74	6.26
		Temperature, 0°C		
310	3.22	1.13	6.62	9.52
366	3.22	1.13	6.62	8.40
417	3.29	1.19	7.06	8.12
455	3.34	1.24	7.28	7.89
511	3.55	1.46	8.53	8.45
		Temperature, +25°C		
256	2.076	0.750	0.79	3.65
313	2.144	0.143	1.52	5.80
368	2.452	0.451	4.80	15.82
432	2.736	0.735	7.82	22.34
486	2.759	0.758	8.67	20.77
541	2.890	0.889	9.47	22.17

coefficient describing the resistance of the underlying solid to the motion of a single adsorbed molecule. The apparent contradiction between expectations and experiment can be cleared up if the influence of the surface inhomogeneity is taken into account. For inhomogenous solid surfaces the mobility of adsorbed molecules should be smaller for low surface concentrations, because the adsorbed molecules are located on more active regions of the surface in this case. In the course of further adsorption molecules are located on less active regions and their mobility increases systematically. Thus we can expect that the friction coefficient is a decreasing function of surface concentration. Introducing the simplest possible concentration dependence of this type $\beta = c/\rho_s$, where c is a constant, we obtain $L_{VV} = \rho_s(c/\rho_s) = c = \text{const}$. We conclude that in the interpretation of the relative independence of L_{VV} of the surface concentration both effects—the concentration dependence of this coefficient and surface inhomogeneity—must be taken into account. The adsorption layer of carbon dioxide studied in this paper has not the properties of a two-dimensional ideal gas. Thus the considerations based on statistical mechanics can not be directly applied to the system studied. We believe however, that the arguments presented explain qualitatively the experimental data obtained.

Finally we want to point out that the influence of surface heterogeneity on the dynamic properties of the adsorbed layer as discussed above does not seem to have a direct relationship with the influence of

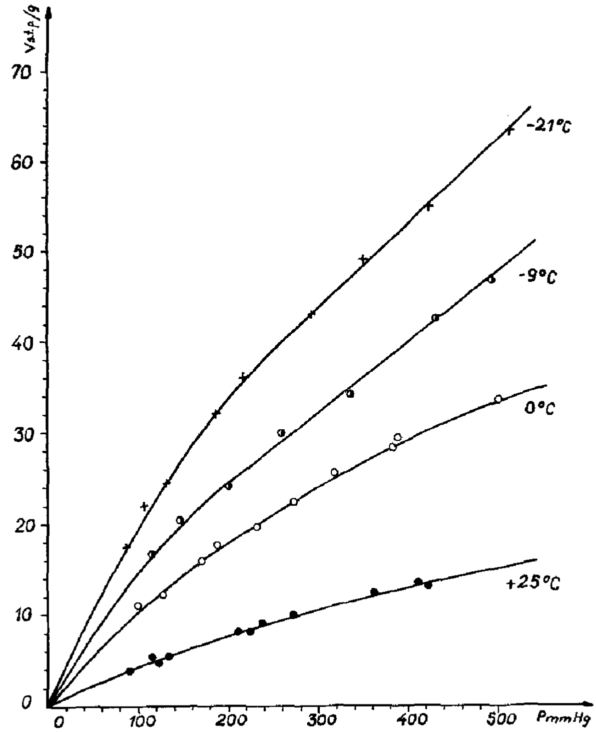

Fig. 3. Adsorption isotherms of CO_2 on active carbon.

surface heterogeneity on equilibrium properties of this layer as demonstrated, for example, by the variation of heat of adsorption with the surface concentration. Comparison of the detailed formulas for the energy of adsorption (*14*) with the formulas for the friction coefficient (*15*) indicate that the dependence of both these quantities on

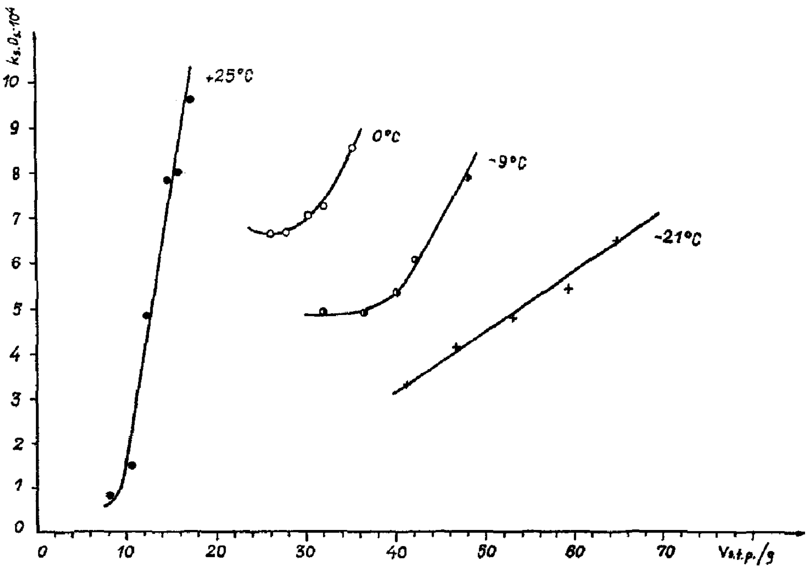

Fig. 4. Dependence of the coefficient K (see text) of the CO_2 concentration on the surface of active carbon.

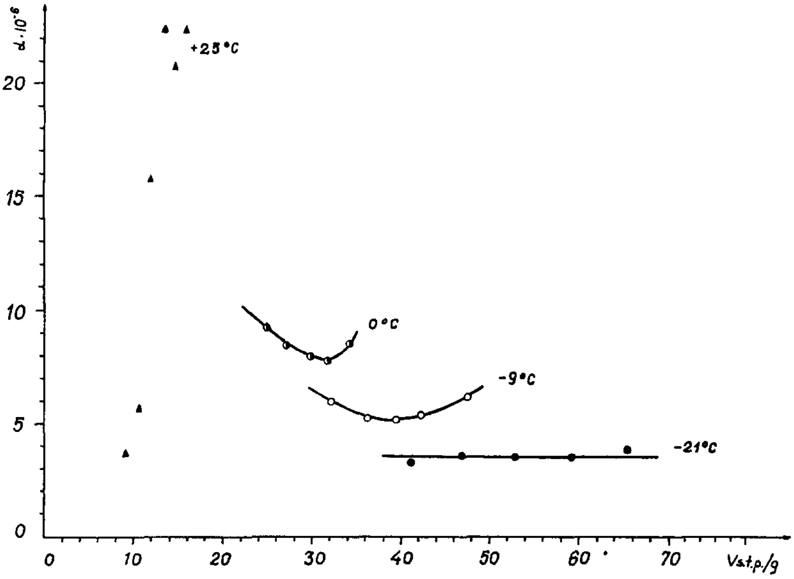

FIG. 5. Dependence of the coefficient α (see text) of the CO_2 concentration on the surface of active carbon.

the molecular parameters (such as intermolecular force constants, density of the solid surfaces and so on) is quite different. If we describe the surface heterogeneity in terms of the variation of elementary moleculular parameters along the surface we can easily see that the influence of this heterogeneity on the two quantities mentioned can be quite different as well.

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