Adsorption of organic substances with different physicochemical properties

2.* The heats of adsorption of freon 13B1 on active carbons

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The linear regions of the adsorption isotherms of freon 13B1 (CF_3Br) on active carbons with different porous structures were studied by gas chromatography at 343—573 K. The Henry's constants were determined, and the isosteric heats of adsorption (Q) were calculated in the region of zero filling. It was established that the Q values for active carbons with different pore size distributions are almost the same and vary within 38—41 kJ mol^{-1}. This coincidence can be explained assuming that the interaction between the adsorbed molecules and the active carbons occurs in the pores whose sizes are comparable with those of the adsorbed molecules.

Key words: Henry's constant, heat of adsorption, active carbon, freon 13B1.

Adsorption processes are finding increasingly wide use. It is of current interest to study the adsorption interactions in freon—active carbon (AC) systems. This interest arises from the necessity to extract toxic organic compounds, in particular, freons, which cause depletion of the atmospheric ozone layer, from air.

The purpose of the present work was to measure the isosteric heats of adsorption of freon 13B1 (CF_3Br) on active carbons in the region of zero filling using milled fractions of the adsorbents.

Experimental

We chose a high-boiling compound, freon 13B1 (CF_3Br),[2] as the object of our study. It has the following parameters: molecular weight, 148.9 g mol^{-1}; b.p., 215.4 K; saturated vapor pressure, 1.43 MPa at 293 K; density of the liquid at 293 K on the equilibrium liquid—vapor line, 1.573 g cm^{-3}; critical temperature, 340.1 K.

Table 1. Parameters of the porous structure of the adsorbents

AC	$W_0{}^0$ / cm^3 g^{-1}	E_0 / kJ mol^{-1}	x_0 / nm	δ / nm
AU-1	0.290	19.8	0.51	0.250
SKT-6A	0.614	21.6	0.46	0.047
FAS-E	0.700	15.5	0.65	0.290
AU-2	0.421	14.2	0.70	0.280
PAU	0.450	27.2	0.37	0.001

We used carbons prepared from various sources as the adsorbents. The parameters of their porous structures presented in Table 1 were calculated according to the procedure in Refs. 3 and 4 from the experimental data on benzene adsorption. As can be seen from the data in Table 1, there are adsorbents with porous structures characterized by either narrow or broad pore volume—size distributions.

Experimental studies were carried out on a Tsvet-100 chromatograph with a flame ionization detector using helium as the carrier gas. The flow rate of the mobile phase was ~0.03 L min^{-1}. The temperature range of the measurements and the masses of the stationary phase (m) are presented in Table 2 for each sorbent. The dose of the compound was 0.1—0.5 cm^3. The adsorption isotherms were corrected for the length of the communicating tubes, time of exit of the nonsorbing component, temperature, and pressure.[5]

The equilibrium characteristics of the freon—AC system were measured in the temperature range 343—373 K on glass columns, 0.5 cm in diameter and 30 cm in length. Metal columns, 0.3 cm in diameter and up to 1 m in length, were used in the temperature range from 500 to 573 K. To pack the columns, a definite fraction of the adsorbent was taken (see

Table 2. Isosteric heats of adsorption (Q) of various ACs

AC	T/K	m/g	d/mm	Q*
AU-1	353—373	3.007	0.615—0.500	38
	533—573	3.208		
SKT-6A	353—373	4.144	0.615—0.500	41
FAS-E	343—373	4.356	1.50—1.25	40
AU-2	443—573	1.284	0.615—0.500	38
PAU	503—573	1.904	0.615—0.500	41

* Q is expressed in kJ mol^{-1}.

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* For part 1, see Ref. 1.

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Table 2), which was usually close to the average fraction of the starting AC. The FAS-E carbon was not separated into fractions.

Results and Discussion

It is known[6] that, for molecular sieves and ACs with a narrow size (x) distribution of the micropore volume (W), which is characterized[3] by δ (the normal distribution dispersion of dW/dx with respect to x; for a narrow distribution, $\delta \cong 0$), the isosteric heat of adsorption of a compound at zero filling by an adsorbent (Q) depends on the parameters of the porous structure, including the characteristic adsorption energy, E_0. The value of E_0 and the micropore size of a sorbent are related by the empirical function,[4] $x_0 = 10/E_0$, where x_0 is the center of the dW/dx distribution. The characteristic value for sorbents with $\delta = 0$ is their micropore size. Naturally, the degree of overlapping of the dispersion fields from the opposite walls of micropores, which depends on x_0 or E_0, determines the value of Q. Ref. 7 reports a linear correlation between the isosteric heats of adsorption of Kr and CF_4 (the diameter of the molecule is $d = 0.55$ nm)[8] and the E_0 parameter for eight active carbons. However, it does not report detailed information on the parameters of the porous structure of ACs nor does it give the values of δ. This does not allow us to classify the active carbons studied in Ref. 7 as sorbents with narrow or broad ($\delta \geq 0.2$ to 0.3 nm) size distributions of the micropore volume.

The equilibrium gas chromatography method has been used[9] to study the effect of the adsorbent porous structure on the adsorption behavior of freons, including freon 13B1. Again, the reported parameters of the porous structure do not allow us to characterize in detail the microporous structure of the adsorbents as uniform or non-uniform. Therefore, we could not reveal the absence or presence of a correlation between Q and E_0.

Of the adsorbents chosen as the objects of the present study, whose parameters are presented in Table 1, only the PAU carbon has $\delta = 0$, *i.e.*, its micropores have almost equal sizes. The other ACs have sorbing pores that vary greatly in size, and the δ values of these carbons differ considerably from zero (see Table 1).

Figure 1 shows the dependences of log V_m (where V_m is the specific retained volume, cm^3 g^{-1}) on $1/T$ for the active carbons studied. One can see in Fig. 1 that the experimental values of log V_m for each AC lie on a straight line, whose slope characterizes the isosteric heat of adsorption of freon 13B1 by a microporous adsorbent at zero filling. Within the accuracy of the experiment, the plots of log V_m *vs.* $1/T$ are parallel to each other for the adsorbents studied. It can be concluded that, for the objects studied, there are no distinct correlations between the isosteric heats of adsorption of freon 13B1 at zero filling and the parameters of the porous structure characterizing the size of the micropores. The Q values presented in Table 2 are the same within the limits of experimental error, even for carbons differing in structure such as PAU and FAS-E (Q = 41 and 40 kJ mol^{-1}, respectively). This suggests that probably the adsorption sites where the first freon molecules are adsorbed at zero filling are energetically equivalent for all ACs studied.

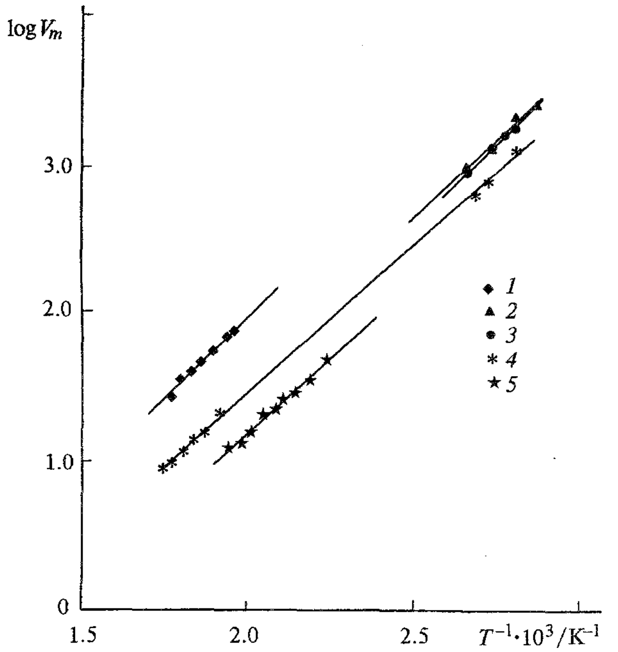

Fig. 1. Dependence of the logarithm of the specific retained volume (V_m) of freon 13B1 on the inverse temperature of the chromatographic column ($1/T$) for active carbons: *1*, PAU; *2*, FAS-E; *3*, SKT-6A; *4*, AU-1; *5*, AU-2.

The results obtained in this work allow us to assume that the molecules of the adsorbate fill the micropores of an active carbon affected by the adsorption fields of the opposite micropore walls. The Q values are the same for all ACs studied, which may be a consequence of the presence of micropores with the same sizes, comparable to the size of the adsorbate molecules, in the structures of the ACs. The diameter of a 13B1 molecule is *ca.* 0.5—0.6 nm.[8] The micropore sizes for the ACs listed in Table 1 were calculated according to the equation[4] $x_0 = 10/E_0$.

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