Dynamics of the adsorption of freons

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The elution adsorption dynamics of some adsorption systems (freon—active carbon) has been studied at two temperatures. The peculiarities of the adsorption dynamics, which are determined by the properties of the adsorption system, have been established. A possibility to calculating elution curves based on the equilibrium adsorption layer model is shown. Preliminary results of the influence of the parameters of the adsorption system on the coefficient of the effective kinetic model are obtained.

Key words: adsorption dynamics, active carbons, freon.

The modeling of elution adsorption dynamics (EAD) makes it possible to optimize adsorption processes involved in absorption, purification, and separation of substances in a wide temperature range. These studies are very important for the investigation of adsorption properties of ozone-hazardous freons, which usually exist within a range of states close to critical.

The adsorptivity of freon 13V1 has been studied previously[1] on microporous active carbon under the conditions of elution adsorption dynamics. The equilibrium adsorption layer model[2] allowed one to satisfactorily describe the data[1] as a whole. The effective kinetic constant used in this model is calculated from the experimental data and cannot be obtained beforehand. In developing the hypotheses determining the dependence of the effective kinetic constant on the parameters and properties of the adsorption system, it is of interest to enlarge the range of adsorptives and adsorbents. The purpose of the present work is to compare the experimental values of the elution dynamics of the adsorption of freon on active carbons with the values calculated using numerical modeling.

Experimental

The procedure of the investigation has been described in detail previously.[3] Freon (8.8 mg) was introduced by a syringe into the flow of a carrier gas (air) in front of an adsorbent placed in a dynamic glass tube (diameter of the adsorbent layer 2.0 cm, velocity of carrier gas 2.2 dm^3 min^{-1}, temperature of experiments 293 and 333 K; length of the adsorbent layer (L) is a constant value). The carrier gas and adsorbent contained almost no water.

The parameters of the structure of the active carbons (limiting adsorption volume of micropores W_0°, characteristic adsorption energy E_0°, half-width of micropores for the maximum of the distribution curve $dW/dx - x_0$, dispersion of the distribution δ, and surface area of mesopores S_{meso}) presented in Table 1 were calculated from data obtained previously.[4]

Adsorption isotherms and their parameters for the adsorption systems were determined by linear chromatography. The procedure was described in detail in Ref. 5. For freon 13V1—AC-1 and freon 13V1—AC-4 systems, whose adsorption isotherms are linear, the values of the Henry constants (K_H) were measured previously.[6] The values of K_H for the two discussed systems and other adsorption systems were calculated by the extrapolation of the linear dependence $\ln K_H - 1/T$ to $T = 293$ and 333 K (Table 2).

The elution curves (EC) obtained at $T = 293$ K for the freon—active carbon systems are presented in Figs. 1—3. The change in the form of EC for different values of L depends on the elution adsorption dynamics. Absolute values of the concentration of the substance (C) behind the layer L, the value of the maximum concentration, and time of its appearance are determined by the properties of the adsorption system. The character of the dependence of the form of EC on L for different adsorption systems is the same. For short adsorbent layers, the concentration of the substance behind the layer that

Table 1. Parameters of the porous structure and granulation of active carbons

AC	d/mm	W_0° /cm^3 g^{-1}	E_0° /kJ mol^{-1}	X_0 /nm	δ /nm	S_{meso} /m^2 g^{-1}
AC-1	0.8—1.2	0.280	19.8	0.51	0.250	74
AC-2	1.0—1.2	0.595	17.1	0.58	0.193	30
AC-3	0.5—0.7	0.465	17.2	0.58	0.300	200
AC-4	1.0—1.2	0.474	28.9	0.35	0.001	15

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Table 2. Values of HETP and Henry constants (K_H) calculated for various adsorption systems

Substance	Adsorbent	T /K	HETP /cm	K_H /dm^3 g^{-1}
Freon 13B1	AC-1	293	0.9	30.0
		333	1.3	2.7
	AC-2	293	0.75	30.0
	AC-3	293	0.7	30.0
	AC-4	293	0.5	42.0
Freon 22	AC-1	293	1.0	39.0
		333	1.3	3.5
Freon 134A	AC-1	293	1.0	43.0
		333	2.0	4.0

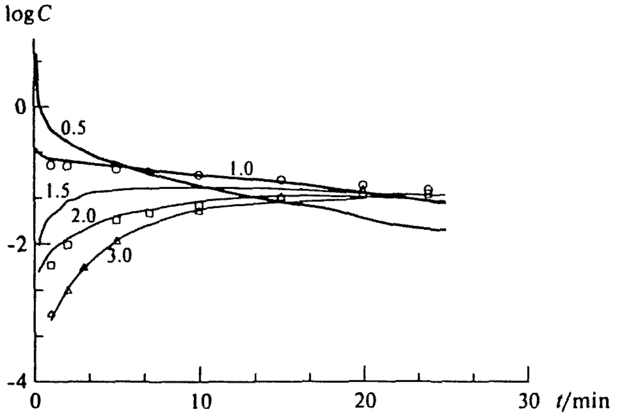

Fig. 1. EC of freon 22 on AC-1, T = 293 K, K_H = 39 dm^3 g^{-1}, L_e = 1.0 cm. In all figures, the numbers designate the length of the adsorbent layer (in cm), the lines indicate the experiment, and the points show the calculation.

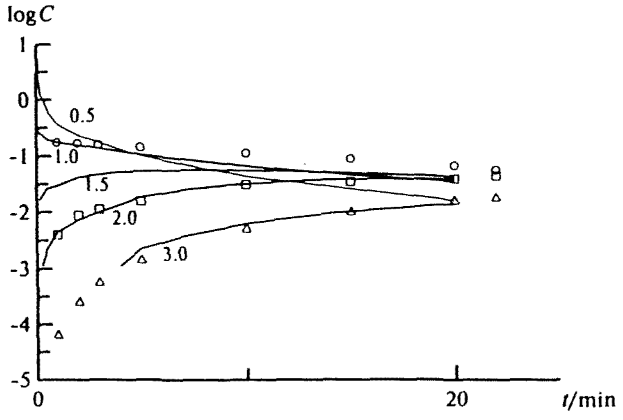

Fig. 2. EC of freon 134A on AC-1, T = 293 K, K_H = 43 dm^3 g^{-1}, L_e = 1.0 cm.

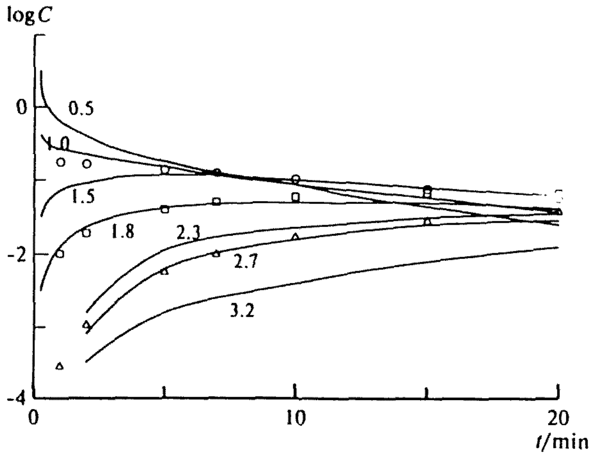

Fig. 3. EC of freon 13V1 on AC-1, T = 293 K, K_H = 30 dm^3 g^{-1}, L_e = 0.9 cm.

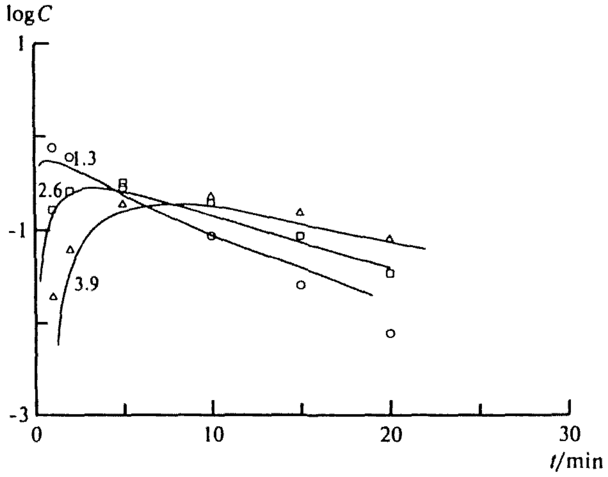

Fig. 4. EC of freon 22 on AC-1, T = 333 K, K_H = 3.5 dm^3 g^{-1}, L_e = 1.3 cm.

is maximum for the given L appears at the initial moment and then decreases slowly. For longer adsorbent layers L, EC are bell-shaped, and the concentration during the dynamic experiment increases slowly with time (t) to some value C_{max} (the time of its achievement is t_{max}) and then decreases slowly.

The results of the experiments at T = 333 K are presented in Figs. 4—6. The shapes of the curves do not change substantially as the temperature increases. For short adsorbent layers, the elution curves have the form of one-sided peaks, which become bell-shaped as L increases. The comparison of EC obtained at T = 293 and 333 K allows one to conclude that the absolute C values behind the layers of active carbons of the same length increase as the temperature increases, the values of C_{max} for equal L also increase, while the time of their achievement (t_{max}) decreases.

Results and Discussion

As seen from Figs. 1—6, the shapes of EC differ from those of the chromatographic peaks observed in analytical high-performance chromatography. As has been shown previously,[1,3,7] short adsorbent layers are characterized by one-sided peaks with blurred lower

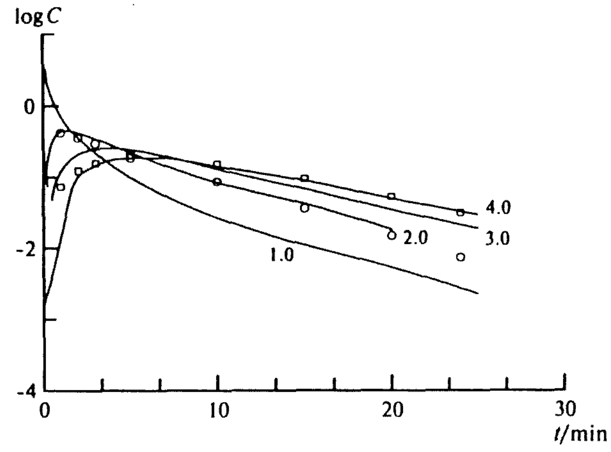

Fig. 5. EC of freon 134A on AC-1, T = 333 K, K_H = 4.0 dm^3 g^{-1}, L_e = 2.0 cm.

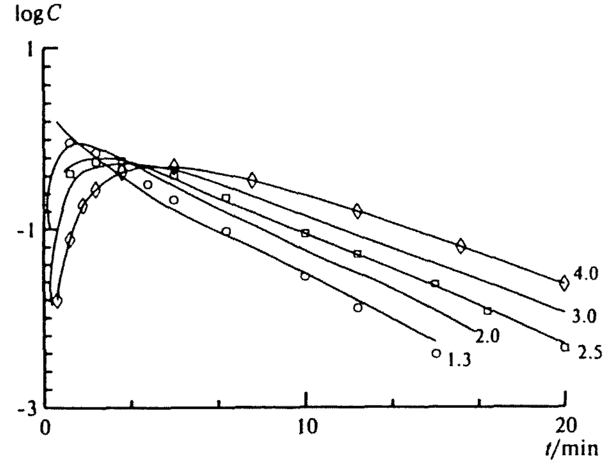

Fig. 6. EC of freon 13V1 on AC-1, T = 333 K, K_H = 2.7 dm^3 g^{-1}, L_e = 1.3 cm.

boundaries. EC in systems with linear and vortex adsorption isotherms have a similar shape.[1,7] Therefore, it is more difficult to estimate the type of adsorption isotherm from the shape of the elution curves than from the curve obtained in the regime of ideal chromatography.[5]

The use of the equilibrium adsorption layer model[2,8] allows one to describe EC for different types of adsorption isotherms. In addition, the solution of the inverse problem of the adsorption dynamics,[8] *i.e.*, the simultaneous determination of the adsorption isotherm and the value of the effective kinetic constant (the equilibrium adsorption layer L_e), is possible in principle on the basis of the model. However, these algorithms have not yet been developed, and, therefore, it is not possible to calculate the numerical value of the effective kinetic coefficient of the model. It is noteworthy that L_e is identical by definition[2] to HETP in the case of a linear adsorption isotherm.

For the calculation of EC in the systems studied, equilibrium adsorption layer models[2] in which the value of the adsorbent layer of the length $l = L_e n$ was determined by the solution of the system and equations of mass balance were used:

$$da_n/df + dC_n/dt = v/L_e[C_{n-l} - C(a)], \qquad (1)$$

where L_e is the effective kinetic constant expressed in length (equilibrium adsorption layer); a_n and C_n are the average values of the adsorption and concentration on the nth intersect of the adsorbent layer, respectively; v is the linear velocity of the mobile phase; C_{n-1} is the concentration of the substance behind the (n − 1)th intersect of the adsorbent layer; and $C(a)$ is the equation of the adsorption isotherm.

The analytical solution of the system of n equations (1) for the linear adsorption isotherm when $C(a) = a/K_H$ is exact, including the cases of short adsorbent layers.[9] In the present work, the numerical solution of the system of n equations (1) obtained in the Turbobasic language using the basic program of the equilibrium adsorption layer model[10] was used. The time of calculation was not greater than 1—2 min. The calculated and experimental EC are presented in Figs. 1—6.

A peculiarity of the mathematical model used is that it is only possible to calculate EC for lengths of adsorbent layers that are multiples of L_e. Therefore, the elution curves for the other adsorbent layers, experimental results for which are presented in the figures, could not be calculated.

As seen from the results presented in Figs. 1—6, the experimental and calculated elution curves agree well. Similar results were obtained for the other adsorption systems. This testifies both to the validity of the mathematical model used and to the reliability of the constants used. The correlation between the elution curves and the length of the adsorbent layers having analytical solutions, has been analyzed previously.[11] The approach suggested for the description of the elution adsorption dynamics can be developed by analyzing the dependence of the adsorption isotherm (K_H) and the effective kinetic coefficient on the physicochemical properties of the substance, the parameters of the porous structure of the adsorbent, and the temperature of the experiment.

Let us analyze the effect of the parameters of the porous structure of active carbons on K_H of the adsorption system for freon 13V1. As follows from the data presented in Table 2, the Henry constants for three active carbons (AC-1, AC-2, and AC-3) at 293 K are approximately equal. In the case of carbon AC-4, the K_H value differs by approximately 40 %, which is likely related to the peculiarity of the microporous structure of this adsorbent, which is characterized by low values of x_0 and δ.

The parameters of the porous structure of adsorbents exert a substantial effect on the value of the effective kinetic constant HETP. HETP is the lowest (0.5 cm) for active carbon AC-4. A decrease in the characteristic adsorption energy E_0 while W_0 remains approximately the same results in a 1.5-fold increase in HETP, which is observed for carbons AC-2 and AC-3, whose HETP values are equal to 0.7 and 0.75 cm, respectively. Variation in the value of the surface of carbon mesopores from 30 to 200 $m^2 g^{-1}$ has no effect on HETP. A decrease in W_0, even with an insignificant increase in E_0, also results in an increase in HETP (for example, for carbon AC-1, HETP = 0.9 cm).

The physicochemical properties of the freons studied have no noticeable effect on HETP. For example, when the saturated vapor pressure changes almost threefold, the values of the effective kinetic coefficients coincide within the calculation error: for the freon 13V1—AC-1 system, HETP = 0.9 cm, while in the case of the freon 134A—AC-1 system, HETP = 1.0 cm.

It follows from the data of Table 2 that an increase in temperature results in an increase in the value of the effective kinetic coefficient HETP. This can be related to an increase in the real velocity of the carrier gas in the tube filled with active carbon rather than to a change in the kinetic parameters of the process as T increases. The increase in HETP as the temperature increases is not the same for different systems. The value of the effective kinetic coefficient reaches a maximum in the system where the adsorbate has the lowest index of saturated vapor pressure (see Table 1). Therefore, the change in HETP is caused not only by the change in the real velocity of the carrier gas, but also by more subtle effects on the adsorption kinetics as a whole.

The systematized values of the effective kinetic coefficient L_e can be used to predict the elution adsorption dynamics of volatile freons on active carbons with various porous structures in a wide temperature range.

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