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Elution and frontal dynamics of adsorption of organic substances on activated carbon

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The elution dynamics of adsorption on activated carbon was studied at various carrier-gas flow rates for a series of organic substances. With the help of the model of the equilibrium adsorption layer that uses the adsorption isotherm described by the theory of volume filling of micropores the outlet curves for the elution and frontal dynamics of adsorption can be adequately predicted. The effective kinetic coefficient and the parameters of the adsorption isotherm were found to be constant for the elution curves calculated both in the elution and frontal regimes of the adsorption dynamics over the whole range of concentrations studied. The effective kinetic coefficient in the mathematical model employed for the systems with microporous adsorbents is independent in fact of the nature of an adsorptive and is mainly determined by the parameters of porous structure of activated carbon and the experimental conditions of a dynamic run.

Key words: adsorption, frontal and elution dynamics of adsorption, adsorption isotherm.

Earlier[1—9] the elution dynamics of adsorption on carbon sorbents has been studied for a series of organic substances. A feasibility of simulation of this process was demonstrated. The model of the equilibrium adsorption layer[10,11] can be applied to calculate the elution outlet curve, that is the concentration of a substance (C) behind the adsorbent layer (L) vs. time (t) curve. This model is a variant of the layer-by-layer method[12] and uses only one kinetic coefficient L_e defined as the equilibrium adsorption layer rather than two kinetic coefficients Δt and ΔL. A solution of the problem involves the calculation of n material balance equations by the method of finite differences.

A procedure for the application of the model of the equilibrium adsorption layer is as follows. A sorbent in the chromatographic column (dynamic tube) is divided conditionally to a finite arbitrary number of elemental layers. The length of each layer is L_e. This value is the effective kinetic coefficient of the adsorption system expressed in the length units.[10] The outlet concentration C_{Le} for a layer L_e at any time is equal numerically to the concentration $C(\bar{a})$, which is the equilibrium average adsorption $\bar{a}$ on this layer. The L_e value, similarly to the height H, which is equivalent to the height of a theoretical plate (HETP), can be represented as the sum of individual terms, which express the constants of the elemental kinetic steps.

The equation of material balance for the equilibrium adsorption layer can be written as follows

$$\frac{d\bar{c}}{dt} + \frac{d\bar{a}}{dt} = \frac{v}{L_e}(c_0 - c_{L_e}),$$

where $\bar{c}$ is the average concentration in the equilibrium adsorption layer, c_0 is the inlet concentration of the substance before the sorbent layer, and v is the linear velocity of the carrier-gas.

For the equilibrium adsorption layer at the inlet of the chromatographic column the direct dynamic problem for any type adsorption isotherms can easily be solved analytically. The expressions describing the outlet curves for the second and following layers are intricate. Therefore, the numerical calculation methods are used to solve such problems.

The adsorption-desorption processes occurring under dynamic conditions in the system volatile substance (Halon)—activated carbon (AC) have been studied and simulated earlier.[4,7,8] It has been shown that the experiments on the elution dynamics of adsorption are described by a linear adsorption isotherm. In this case, the problem of numerical simulation of the outlet curves for the elution dynamics of adsorption with the use of the model of the equilibrium adsorption layer is substantially simplified since one can calculate the equilibrium ad-

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sorption layer L_e, which coincides with the HETP value under the conditions of the linear non-equilibrium chromatography. When dynamic processes in the adsorption systems with non-linear adsorption isotherms are treated, the L_e values are determined by successive solution of the direct problem of adsorption dynamics for various L_e.[6,9] No procedure to calculate the L_e value for the systems with adsorption isotherms of any type has been elaborated.

Of particular interest is to calculate the outlet curves for the dynamics of adsorption under both elution and frontal regimes using the same mathematical apparatus for the same adsorption systems and experimental conditions. The existing semiempirical models, which are commonly applied for the frontal dynamics of adsorption, do not allow the calculation of the outlet curves when the same adsorption system is operative under the elution regime. We have shown[8] that it is possible to predict both the elution and frontal curves of the dynamics of adsorption for Halon 22 on AC based on the model of the equilibrium adsorption layer with the use of the same L_e value and the same equation describing the adsorption isotherm. Outlet curves in the elution regime were calculated for the adsorption isotherm that fits a linear Henry's isotherm. The L_e value was calculated by the method of moments[13,14] from experiments in the elution regime. Then this numerical value was used to calculate the frontal outlet curves. The adsorption isotherm for the frontal experiments at small concentrations and, correspondingly, small coverages of AC was derived from the same linear adsorption isotherm. At high coverages of AC the isotherm was described by the Dubinin—Radushkevich (DR) equation,[15] *i.e.*, by a convex isotherm. Calculated values and experimental results are in good agreement.

The objective of this work is to evaluate the feasibility of the model of the equilibrium adsorption layer for solving the direct problem of the adsorption dynamics in the frontal and elution variants for a wider range of substances and to study the effect of the air-vapor flow rate and physicochemical properties of adsorptives studied on the L_e value.

Experimental

The experimental procedure for the elution dynamics of adsorption has been described earlier.[1—3] The experimental conditions are presented elsewhere.[1—9] The following values of flow rate of the carrier-gas (v) were used: 0.50, 0.95, 1.70, and 2.20 L min^{-1}. The temperature of experiments was 293 K. The lengths of the AC layer (L) are shown in captions to Figs. 1—4. The initial concentrations in the frontal regime[16] (C_0) were 2.0 mg L^{-1} for chloroethane and benzene and 3.7 mg L^{-1} for hexane.[17,18] The dose introduced (q) in the experiments in the elution regime was varied within 8.8—20 mg. Physicochemical parameters of adsorptives are presented in Table 1.

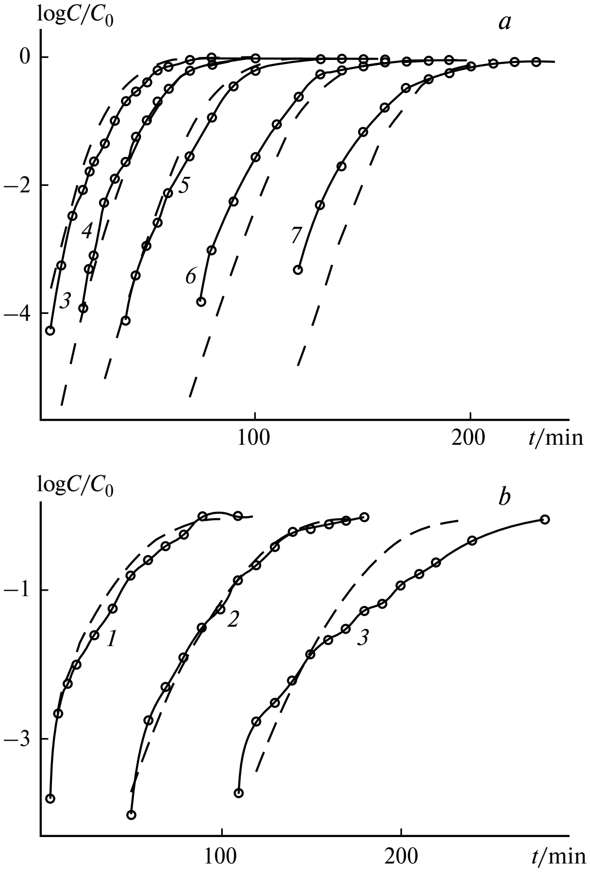

Fig. 1. The outlet curves for the frontal adsorption dynamics for chloroethane (*a*) and benzene (*b*) over different layers of AC[16] at v = 0.95 L min^{-1}, C_0 = 2 mg L^{-1} and the AC layer length of 0.5 (*1*), 1.0 (*2*), 1.5 (*3*), 2.0 (*4*), 2.5 (*5*), 3.0 (*6*), and 4.0 cm (*7*). Hereinafter solid lines are experimental data and dotted lines are calculation findings.

Industrial steam-activated carbon with the limiting adsorption volume of 0.280 cm^3 g^{-1}, the characteristic energy of adsorption of 19.8 kJ mol^{-1}, and the surface area of mesopores of 74 m^2 g^{-1} was used as the adsorbent.

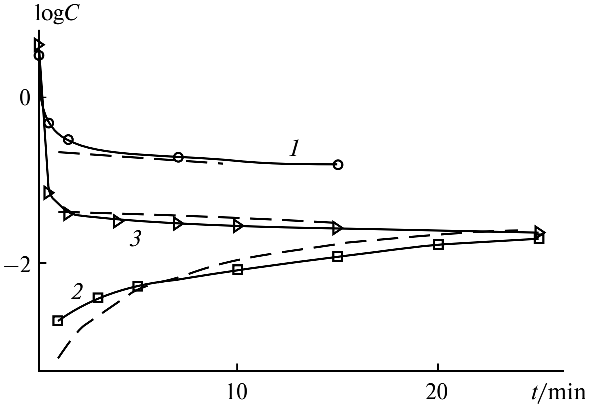

Fig. 2. The outlet curves for the elution adsorption dynamics for chloroethane over different layers of AC at v = 1.70 L min^{-1}, q = 20 (*1*, *2*) and 10 mg (*3*), L = 0.75 (*1*, *3*) and 1.5 cm (*2*).

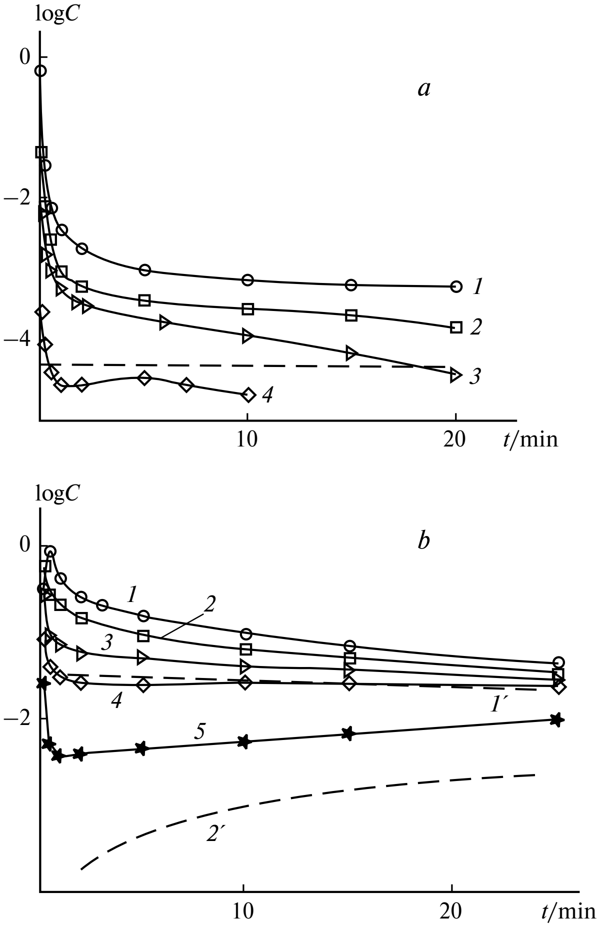

Fig. 3. The outlet curves for the elution adsorption dynamics for benzene (*a*) and chloroethane (*b*) over different layers of AC at $v = 2.2$ L min^{-1}, $q = 8.8$ mg and the AC layer length of 0.3 (*1*), 0.5 (*2*), 0.7 (*3*), 1.0 (*4*), and 1.2 cm (*5*); *1′*, *2′* are the calculated values at the AC layer length of 1 and 2 cm, respectively.

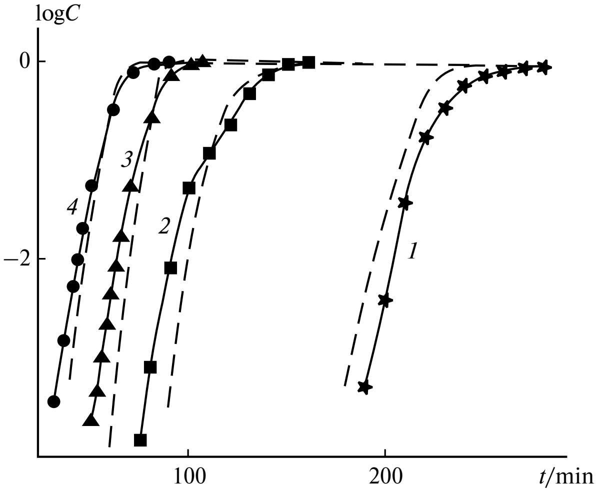

Fig. 4. The outlet curves for the frontal adsoption dynamics for hexane over the AC layer of 2 cm length at $v = 0.5$ (*1*), 0.95 (*2*), 1.6 (*3*), and 2.0 L min^{-1} (*4*).

Table 1. Physicochemical properties of adsorptives

Substance	M	B.p. /°C	Parachor	C_s /mg L^{-1}
Benzene	78.1	80.1	207	321
Hexane	86.1	68.7	271	571
Chloroethane	64.5	12.3	151	3500
Halon 13B1	148.9	−57.8	155	87500
Halon 134A	102	−26.5	141	24000
Halon 22	86.5	−40.8	128	33500
Halon 113	187.4	47.5	221	2800
Bromomethane	94.9	3.6	124	9300

Note. The following designations are used: M is the molar weight, C_s is the concentration of the saturated vapor of the organic substance at 20 °C.

Variations in the shape of the elution outlet curves as a function of L and v (see Figs. 1—4) obey the regularities found previously.[1—9]

Results and Discussion

The reported[16] findings on the frontal dynamics of adsorption in the systems chloroethane—AC and benzene—AC were obtained on the AC sample, which is similar to the AC sample studied in this work in terms of the pore structure parameters. On the basis of the model of the equilibrium adsorption layer we calculated the outlet $C(t)$ curves for the above adsorption systems. The L_e value was determined by successive solution of the direct problem for the adsorption dynamics at several L_e values. An accuracy of the determination of the kinetic coefficient is equal to that of a dynamic experiment and is at most 10—15%. For chloroethane and benzene $L_e =$ 0.5 cm at $v = 0.95$ L min^{-1}. The adsorption isotherm was given by the DR equation, and the parameters of the AC porous structure were used. Within the accuracy limit, a coincidence of the experimental outlet curves and those derived from the model of the equilibrium adsorption layer for the frontal dynamics of adsorption is obtained for the chloroethane—AC and benzene—AC systems involving different L ($v = 0.95$ L min^{-1}) (see Fig. 1). Figure 2 shows the results of the calculation of the outlet curves in the elution regime performed according to the model of the equilibrium adsorption layer with the use of $L_e = 0.5$ cm and the DR equation of the adsorption isotherm for chloroethane. As can be seen, the experimental elution outlet curves and the calculated curves are in good agreement. Hence, it is possible to predict the adsorption dynamics in the systems chloroethane—AC and benzene—AC both under the frontal and elution regimes on the basis of the same mathematical model, using the same adsorption isotherm equation and effective kinetic coefficient.

Table 2. The effective kinetic coefficients (L_e), adsorption systems, and experimental conditions

v/cm min^{-1}	L_e/cm	Substance	Regime	Shape of AI
700	1.0	Halon 13C1	E	L
		Halon 134A	E	L
		Halon 22	E	L
		Chloroethane	E	C
		Benzene	E	C
		Bromomethane	E	C
		Hexane	E, F	C
500	0.75	Halon 22	E	L
		Chloroethane	E	C
		Benzene	F	C
		Hexane	F	C
300	0.5	Halon 22	E, F	L, L + C
		Chloroethane	E, F	C
		Benzene	F	C
		Hexane	F	C
160	0.5	Hexane	F	C
1100	1.5	Halon 113	F	C

Note. The following designations are used: E and F are elution and frontal regime, respectively; L and C are linear and convex— shapes of the adsorption isotherm, respectively.

To elucidate the influence of v on the L_e value, we carried out a set of experiments on the adsorption dynamics in the elution regime at v = 2.2 L min^{-1} (see Fig. 3). In calculations of the outlet curves, the DR adsorption isotherm was used. The effective kinetic coefficient for both adsorption systems proved to be 1.0 cm. Because of a low sensitivity of the experimental procedure, it is difficult to measure the outlet curves experimentally at L > 1.0—1.2 cm. Nevertheless, the outlet curves for the adsorption dynamics can be calculated with the use of the model of the equilibrium adsorption layer.

As the experiments and calculations showed, L_e increases with increasing v. Table 2 presents the effective kinetic coefficients obtained in the experiments on the adsorption dynamics in both the frontal and elution regimes at one temperature (293 K) for the adsorption systems with the same adsorbent and different organic substances whose physicochemical properties vary in a wide range. Also presented are the linear velocities of a vapor-gas flow (v), the type of adsorption isotherm, and the character of the experiment, in which the corresponding numeral L_e value was determined.

Examination of the data gives evidence that the nature of the organic substance does not affect the value of the effective kinetic coefficient derived from this model. The L_e value is the same for all substances studied in this work at the same v value. In the system carbon black—organic substance,[6] the effective kinetic coefficient depends on the properties of an adsorptive. The L_e values for benzene and chloroethane differ by a factor of 1.5, although such a dependence was not revealed for microporous sorbents.

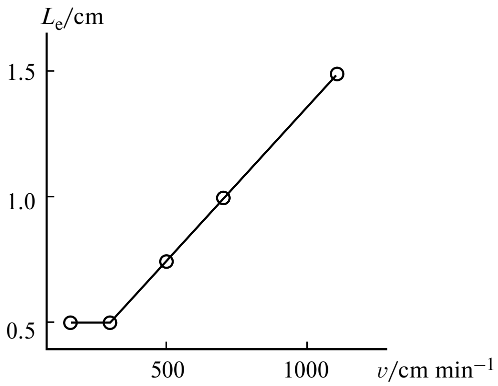

Fig. 5. The effective kinetic coefficient (L_e) *vs.* the carrier-gas flow rate (v).

A L_e *vs.* v plot is similar to that for HETP *vs.* carrier-gas flow rate (Fig. 5). The L_e value does not change in fact in the range v = 160—300 cm min^{-1} and then increases with the linear velocity of the carrier-gas. One can conclude from the examination of the reported data[7] that a similar dependence of L_e on v is valid for other activated carbons.

With the use of the above feature a similar calculation was carried out for the hexane—AC system for which the experimental data on the frontal adsoption dynamics are available.[17,18] In calculations based on the model of the equilibrium adsorption layer, the parameters of the hexane adsorption isotherm were introduced that were derived from the DR adsorption isotherm with allowance for the parameters of the AC porous structure and the physicochemical constants of hexane. Based on the data of Table 2 the value of the effective kinetic coefficient was chosen. The findings of experiments and calculations are presented in Fig. 4. It is obvious that the calculation method outlined above makes it possible to solve the direct problem of the adsorption dynamics for various organic substances and conditions of dynamic runs with satisfactory accuracy. In addition, the shape of the outlet curves for the elution and frontal dynamics of adsorption can be predicted.

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