Elution dynamics of adsorption of Chladon 113 and methyl bromide on active carbons

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The elution dynamics of adsorption of Chladon 113 (at high contents of the adsorptive) and methyl bromide on active carbons with different lengths of the layer was studied. The adsorption isotherms were described by the equation of the theory of volume filling of micropores. The elution curves were calculated using the model of the equilibrium adsorption layer. The effective kinetic constant calculated in the framework of the model is 1.5 cm for Chladon 113 at a linear velocity of vapor-air flow of 1250 cm min^{-1} and 1.0 cm for methyl bromide at the velocity of 700 cm min^{-1}.

Key words: elution adsorption dynamics, Chladon 113; methyl bromide; elution curves.

The adsorption dynamics of halogen-containing hydrocarbons (gaseous freons on active carbons (AC)), when the adsorption isotherm (AI) is linear, is sufficiently well described in the literature.[1,2] It is of interest to study the adsorption dynamics of halogen-containing hydrocarbons with adsorption isotherms obeying more complex equations. In this experimental work, we studied the elution adsorption dynamics (EAD) of Chladon 113 (Freon 113) in the liquid state under normal conditions and methyl bromide on industrial active carbons.

Experimental

The physicochemical properties of the substances under study are presented below.[3]

Substance	M	B.p. /K	C_s /mg L^{-1}	ρ /g cm^{-3}
Chladon 113	187.4	320.7	2800	1.587
Methyl bromide	94.9	276.8	9300	1.676

Note: ρ is the adsorbent density.

Industrial active carbons with parameters of porous structure determined by a standard method[4] and presented below served as adsorbents.

	W_0 /cm^3 g^{-1}	E_0 /kJ mol^{-1}	S_{meso} /m^2 g^{-1}	δ /nm
AC-1	0.421	14.2	85	0.282
AC-2	0.280	19.8	74	0.250

Note: S_{meso} is the surface area of mesopores of AC, and δ is the dispersion of the micropore volume size distribution for AC.

The procedure of studies in the elution regime of adsorption dynamics was described in the previously published work.[1] According to this procedure, a certain amount of the substance q was injected with a constant velocity of the carrier gas v in the adsorbent layer (with the length l) packed in a dynamic tube with the diameter d. Air served as the carrier gas. A change in the concentration of the substance (C) with time (t) behind the adsorbent layer was monitored by a flame-ionization detector.

The elution dynamics of the Chladon 113 adsorption on industrial AC-1 was studied under the following conditions: v = 0.8 L min^{-1}, d = 0.9 cm, q = 320 mg; the length of the AC layer was varied within 1.5—4.5 cm. The conditions for adsorption of methyl bromide on AC-2 were: v = 2.2 L min^{-1}, d = 2.0 cm, q = 8.8 mg, the length of the AC layer varied

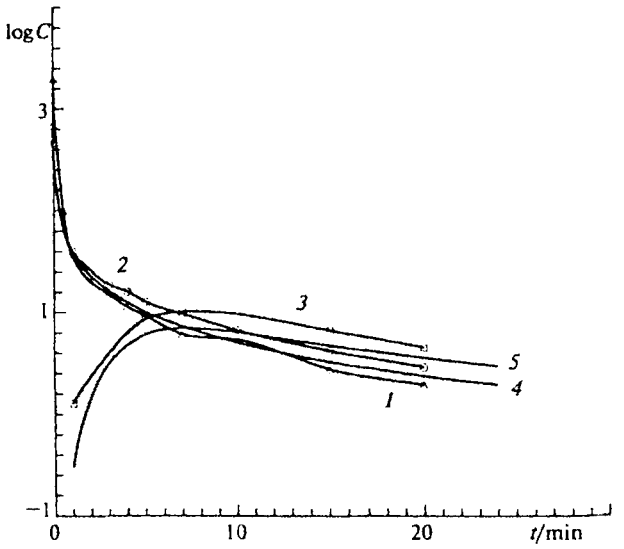

Fig. 1. Elution curves of Chladon 113 at different lengths of the AC-1 layer (in cm): 1.5 (*1*), 3.0 (*2*, *4*), and 4.5 (*3*, *5*). *1*—*3* are experiments, and *4*, *5* are calculations.

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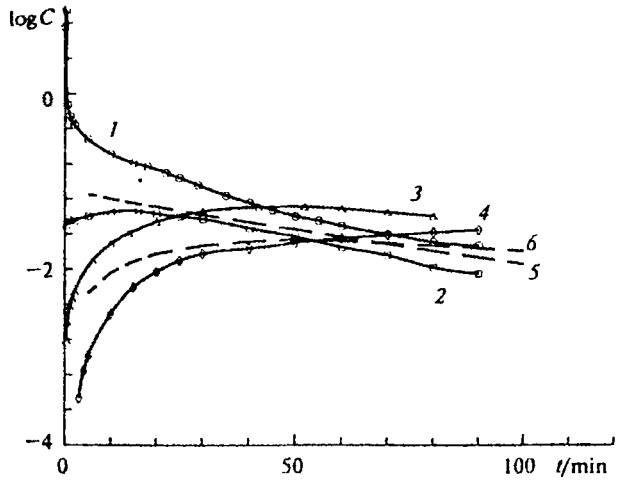

Fig. 2. Elution curves of methyl bromide at different lengths of the AC-2 layer (in cm): 0.5 (*1*), 1.0 (*2*, *5*), 1.5 (*3*), and 2.0 (*4*, *6*). *1*—*4* are experiments, and *5* and *6* are calculations.

within 0.5—2.0 cm. Experiments were carried out at 293 K; the air flow and adsorbent were virtually dry.

Experimental elution curves (EEC) for Chladon 113 on AC-1 and methyl bromide on AC-2 are presented in log$C$—t coordinates in Figs. 1 and 2, respectively.

Results and Discussion

The main features of the elution adsorption dynamics, including the dependences of the shapes of the elution curves on L for adsorption systems with arbitrary adsorption isotherms, were predicted in Ref. 5. These predictions were experimentally confirmed mainly for linear adsorption isotherms.[1,2,6—8] The differences of the present study with the Chladon 113—AC-1 system from the earlier experiments lie in the substantially greater amount of the substance introduced and the considerable deviation of AI from the linear form. These differences determine the shape of the elution curves. In the experiments with L = 1.5 and 3.0 cm, the elution curves of Chladon 113 are skewed peaks with extended rear tailing; and for the AC layer with L = 4.5 cm, they are bell-shaped. In the case of methyl bromide, the dose introduced is considerably less, and a skewed peak is typical of the 0.5-cm layer; while in the experiments with L = 1.0—2.0 cm, the elution curves are blurred with the extended front and rear signals.

An adsorption isotherm for adsorptives on AC should be described for the theoretical calculation of the elution curves. For this purpose, we used the AI equation of the theory of volume filling of the micropores (TVFM):[4]

$$a = a_0 \exp\left(-(A/\beta E_0)^2\right), \quad (1)$$

$$a_0 = W_0/V^*, \quad (2)$$

where a/mmol g^{-1} is the amount adsorbed; a_0/mmol g is the adsorption capacity; V^*/cm^3 mmol^{-1} is the molar volume of the adsorbed phase; W_0/cm^3 g^{-1} is the total volume of the micropore system; $A = RT\ln(C_s/C)$/kJ mol^{-1} is the differential molar work of adsorption; C and C_s/mg L^{-1} are the concentrations of the substance and saturated vapor of the adsorbate at the temperature of the experiment, respectively; E_0/kJ mol^{-1} is the characteristic energy of benzene adsorption; and β is the scaling factor (calculated as the ratio of the parachor of the adsorbate to that of benzene taken as the standard adsorbate).

It is noteworthy that this approximation of AI by the equation of TVFM contradicts neither the theory nor the experiment,[4] because the concentrations under study vary within 10^3—10^{-1} mg L^{-1} ($C/C_s = 3\cdot10^{-4}$—$3\cdot10^{-1}$), and the value of the adsorptivity, which is equal to the exponential part of Eq. (1), is within the 0.20—0.94 range.

The elution curves were calculated by the model of the equilibrium adsorption layer.[9] For this purpose, one should know the value of the effective kinetic coefficients of the model, which is termed as the equilibrium adsorption layer (L_e), and parameters of the dependence $a = f(C)$ of the adsorption system. The effective kinetic constant L_e is expressed in units of length. The calculations using the mathematical model are described in detail in the previously published works.[2,6—8]

For both series of experiments, the L_e value was determined by the successive solution of the direct problem of adsorption dynamics for several values of the given coefficient. In the calculations for the experiments with Chladon 113, the L_e value was first equalized to 0.5 cm and then increased with an increment of 0.1—0.2 cm to 4.5 cm; in the experiments with methyl bromide, L_e was increased to 2.0 cm.

The calculation program in Turbobasic using a personal computer was modified for the calculations with Chladon 113, since the q value exceeded the adsorption capacity of AC layers up to the l values equal to 1.5 cm. Therefore, in calculations where L_e is less than 3.0 cm the substance was dosed by two pulses at an interval of 1 s. The value of the first pulse was 98% of the adsorption capacity of the AC layer L_e, while the value of the second pulse was equal to the difference between q and the first pulse. In calculations where L_e = 1.5 cm, the first and second pulses were equal to 0.65 q and 0.35 q, respectively.

The calculations in the experiments with Chladon 113 differs from those with methyl bromide and the adsorption systems studied previously[1,2,6—8] where the value of the substance pulse did not exceed 10% (and more often, 3—5%) of the total capacity of the AC layer chosen as L_e.

The best coincidence between the experimental and calculated elution curves was observed at L_e = 1.5 cm for the Chladon 113—AC-1 system and L_e = 1.0 cm for the methyl bromide—AC-2 system. These values of

L_e were accepted as parameters of dynamic processes for the adsorption systems studied and specified experimental conditions.

The study performed has confirmed the possibility to use the mathematical model for calculating the elution dynamics of adsorption of different halogen-containing hydrocarbons (including those in the liquid state under normal conditions), whose adsorption isotherms on AC are described by a sufficiently complex equation and differ substantially from the linear form. This model makes it possible to calculate elution curves under conditions of greater doses of the substance introduced in the AC layer.

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