

Letters to the Editor

Elution on adsorbent beds of short length. Analytical solution

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Earlier,¹ equations describing elution dynamics of adsorption were considered and the possibility of analytical solution of the direct problem for integer number of relative length of the adsorbent bed in column was verified. Later,² the elution curve was analysed

$$c/c_0 = \exp(-bt) \cdot (bt)^{n-1} / (n-1)! \quad (1)$$

where $c = c(n, t)$ is the concentration in the coordinate of the relative length equal to n ; t is the time; c_0 is the maximum concentration monitored by the outlet elution curve for $n = 1$ determined by the amount of substance introduced; $n = L/L_e$ is the relative length of adsorbent bed in the column; L is absolute length of the adsorbent bed; L_e is an effective kinetic constant (an equilibrium adsorption layer)³; $b = v/L_e \cdot (1 + \Gamma)$, v is the linear rate of a mobile phase; Γ is the constant of Henry's linear adsorption isotherm.

Equation (1) is known in the plate theory⁴ and is used in chromatography in approximation $n \rightarrow \infty$, when the concentration function is described by the Gaussian curve. The possibility of using integer number in Equation (1) including low n values was proved in many studies.^{2,5–7}

In the real adsorption dynamics, the adsorbent beds with relative length expressed as real numbers are used. Therefore, the problem of description of elution dynamic processes on the short length columns including membrane thin layers remains topical. The present study is

aimed at extending the application of Equation (1) to the real n values.

The experimental results⁷ analysed in the present study were obtained according to the procedure earlier described.⁵ The investigated substance was freon 13B1 (CF₃Br). Freon (8.8 mg) was fed *via* a syringe to the glass tube with the adsorbent in a stream of air (adsorbent bed diameter 2.0 cm, carrier gas flow rate 2.2 dm³ min⁻¹ at a temperature of 333 K). The change in freon concentration with time behind the adsorbent bed was controlled by the flame-ionization detector.

The characteristics of the structure of gas-vapor activated carbon AU-1 were calculated in accordance with the earlier obtained data:⁸ the total adsorption volume of micropores 0.280 cm³ g⁻¹, characteristic adsorption energy 19.8 kJ mol⁻¹, mesopores surface 74 m² g⁻¹. The value of the Henry's constant for the system freon 13B1–AU-1, the isotherm of which gave a linear plot at the studied temperature, was earlier evaluated from gas chromatographic measurements.⁹

When the inverse problem was solved by the method of moments^{2,5–7}, the possibility of calculations of the constants L_e and Γ for the short length columns with fractional n values was demonstrated. To determine factorial $(n-1)!$ value at real $n > 0$ suggestion was made to calculate area under the curves (1) and to compute their ratio to the area integrable for integer n values, when

$$\int_0^\infty [\exp(-bt) \frac{(bt)^{n-1}}{(n-1)!}] dt = 1/b. \quad (2)$$

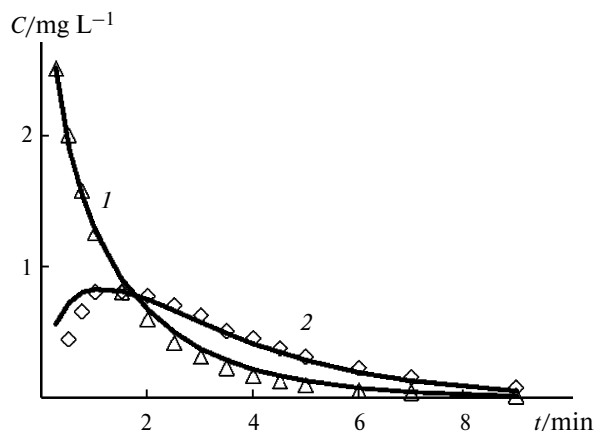


Fig. 1. Elution curves of freon 13B1 for the layers of activated carbon with relative lengths of 0.77 (1) and 1.54 (2). Dots denote experimental data, lines denote data calculated by Equation (1).

Integral of function (1) coincides with the gamma function known in mathematics, its values are tabulated for arbitrary n values.¹⁰ When Equation (1) is used for practical purposes, the value of factorial $(n - 1)!$ of real number including the range $0 < n < 1$ can be approximately estimated from the experimental curves or from areas under the curves (1) calculated at low Δt values.

The elution curves of the freon 13B1 experimentally obtained⁷ and calculated by Equation (1) with allowance for the factorial $(n - 1)!$ are given in Fig. 1. The experimental conditions: adsorbent bed lengths are 1 and 2 cm. Constants calculated by the method of moments: $L_e = 1.3$ cm, $\Gamma = 2.7$ dm³ g⁻¹ or $\Gamma = 1120$ and $b = 0.48$ min⁻¹. The adsorbent bed relative lengths are $n = 0.77$ and 1.54. The value of factorial $(n - 1)!$ is taken to be 1.15 (in the study,¹⁰ the value of 1.17 is given) for $n = 0.77$. For $n = 1.54$, the factorial value was calculated from the areas ratio by Equation (2) and is equal to 0.89, which completely corresponds to literature data.¹⁰ The experimental and theoretical data were obtained at low values of relative lengths of adsorbent bed, when the shape of elution curves is considerably different from the ideal Gaussian curve.^{1,2,5-7}

The experimental curves are in agreement with theoretical curves (see Fig. 1), which is confirmed by equal

values of the adsorption and kinetic constants calculated from these curves by the method of moments.

Thus, Equation (1) is a solution of a direct problem of elution dynamics of adsorption at the arbitrary relative lengths of adsorbent beds and can be applied to optimize the operating conditions of compact cleaning filters and membranes in the currently used technologies.

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