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CHEMISTRY AND TECHNOLOGY OF RARE, TRACE AND RADIOACTIVE ELEMENTS

Separation of Liquid Mixtures by Dynamic Countercurrent Cyclic Extraction

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Abstract—This paper deals with a new method of dynamic countercurrent cyclic extraction. Each cycle consists of two light- and heavy-phase motion stages. The time of each phase is variable and must be specified for each process cycle. A mixture of components to be separated is injected with one of the phases during a certain time period, which does not exceed the time of this phase motion stage in the initial process cycle. A mathematical model of dynamic countercurrent cyclic extraction is developed. Some analytical relationships for calculating the separation of liquid mixtures by this method are derived. The proposed dynamic regime of extraction has been established to considerably (by several times) increase the operational efficiency of extraction units. A comparison of the experiment and theory demonstrates satisfactory agreement between them.

Keywords: countercurrent cyclic extraction, preparative solid support-free liquid–liquid chromatography, mathematical modeling

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INTRODUCTION

This work continues the studies performed in the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences on the creation of new more efficient extraction processes for the separation, purification, and concentration of liquid mixture components. These studies are performed in the two fields: (1) the development of dynamic (nonstationary) extraction methods combining the advantages of countercurrent extraction and solid support-free liquid–liquid chromatography [1–13], and (2) the development of extraction processes based on the principle of liquid membranes [14–23]. This paper reports the results of studies in the first direction and is devoted to the countercurrent cyclic processes for the extraction-chromatographic separation of liquid mixtures.

In contrast to the methods of classic chromatography, the so-called stationary phase in solid support-free liquid–liquid chromatography is mobile, as it is retained inside of a chromatographic device in a free (mobile) state by centrifugal forces [24–32] or viscosity and surface tension forces [1, 5–7, 9, 10] instead of being immobilized on a stationary solid support. A chromatographic device represents a centrifuge with an installed chromatographic column in the first case and a series of vertical columns divided into cells with horizontal perforated trays in the second case. The mobility of both liquid phases in these devices enables the creation of new more efficient cyclic [2–5] and countercurrent cyclic [1, 7, 11, 12, 27–30] methods for separating liquid mixtures. Each cycle of a countercurrent cyclic process consists of the two stages, i.e., a (1) first stage of phase motion and (2) second stage of phase motion. The analysis of countercurrent cyclic chromatography processes under the conditions when a mixture of components to be separated (sample) is fed into the middle zone of a series of equilibrium cells was performed earlier [7, 11, 12]. In this case, the time of phase motion stages was kept constant in all of the process cycles.

This paper considers a cyclic process with a variable time of phase motion stages. In this countercurrent cyclic process, a sample reciprocates in an extraction-chromatographic device (column) until the separation of components is attained. This increases the path of the sample in the column (it is likely to be elongated) and, thus, the efficiency of the separation process. Since the separation of components during the motion of the sample inside the column is accompanied by the broadening of peaks due to the interphase mass exchange and longitudinal mixing, it is necessary to decrease the time of phase motion stages from cycle to cycle to retain a sample inside the column during a certain number of cycles.

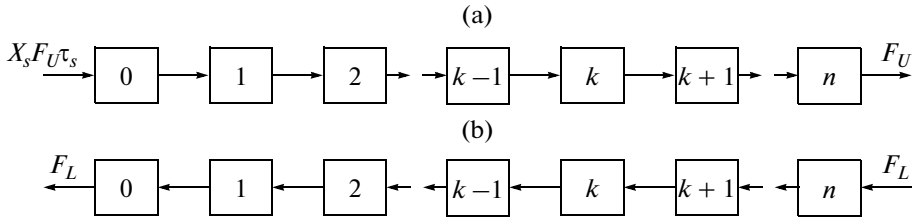

Fig. 1. Flowsheet of the dynamic countercurrent cyclic extraction process: (a) process beginning, stage of light-phase motion, (b) stage of heavy-phase motion.

THEORETICAL

To implement a new countercurrent cyclic process with a variable time of phase motion stages and to select the optimal conditions for certain liquid-mixture separation purposes, it is necessary to have a mathematical description. To accomplish this, let us use the modified equilibrium cell model, which takes into account the effect of longitudinal mixing and mass exchange on the process of separation [2, 3, 7, 8, 12, 31–34].

Let us perform an analysis of the countercurrent cyclic process with a variable time of phase motion stages for the conditions, when a sample is continuously fed with the flow of one phase in the first process cycle during a certain time period (Fig. 1). When a sample is fed with the light-phase flow at the beginning of a series of equilibrium cells (into cell no. 0), the mathematical model of the process can be written according to Fig. 1 as the following set of equations in dimensionless variables.

First Cycle

Stage of light-phase motion (Fig. 1a)

$0 \le t \le t_s$:

$$\frac{1}{a}\frac{dX_0}{dt} = X_S - X_0, \quad (1)$$

$$\frac{1}{a}\frac{dX_k}{dt} = X_{k-1} - X_k, k = 1, 2, \ldots, n, \quad (2)$$

$t \ge t_s$:

$$\frac{1}{a}\frac{dX_0}{dt} = -X_0, \quad (3)$$

$$\frac{1}{a}\frac{dX_k}{dt} = X_{k-1} - X_k, k = 1, 2, \ldots, n, \quad (4)$$

$$t = (\tau F_U)/V_c.$$

Stage of heavy-phase motion (Fig. 1b)

$$\frac{1}{aK_D}\frac{dY_k}{dt} = Y_{k+1} - Y_k, k = 0, 1, 2, \ldots, n-1, \quad (5)$$

$$\frac{1}{aK_D}\frac{dY_n}{dt} = -Y_n, t = \tau F_L/V_c. \quad (6)$$

Second and Subsequent Cycles

Stage of light-phase motion (Fig. 1a)

$$\frac{1}{a}\frac{dX_0}{dt} = -X_0, \quad (7)$$

$$\frac{1}{a}\frac{dX_k}{dt} = X_{k-1} - X_k, k = 1, 2, \ldots, n. \quad (8)$$

$$t = (tF_U)/V_c.$$

Equations (5) and (6) remain valid for semiperiods of heavy-phase motion.

In Eqs. (1)–(8), the following notations are accepted:

$$a = \frac{N}{1 - S + SK_D},$$

and

$$S = \frac{V_L}{V_L + V_U} = \frac{V_L}{V},$$

where $X = \frac{x}{\bar{x}}$ and $Y = \frac{y}{\bar{x}}$ are the dimensionless concentrations in the phases; $\bar{x} = \frac{Q}{V} = \frac{x_sF_U\tau_s}{V}$ is the average concentration in a column; $Q = x_sf\tau_s$ is the quantity of a component fed with the light phase; x is the concentration of a component in the light phase; y is the concentration of a component in the heavy phase; τ is the time; x_s is the concentration of a sample in the light phase during its injection for the time $\tau_s \le \tau_{1U}$; τ_{1U} is the first stage (light-phase motion) time in the first cycle; $t = \frac{\tau F_U}{V}$ is the dimensionless time in the light-phase motion semiperiod; $t = \frac{\tau F_L}{V}$ is the dimensionless time in the heavy-phase motion semiperiod; $t_s = \frac{sF_U}{V}$ is the dimensionless sample injection time; $K_D = y/x$ is the distribution coefficient; k is the current cell number (Fig. 1); $N = 1 + n$ is the number of cells in a series; V_U and V_L are the volume occupied by the light and heavy phases in an apparatus, respectively; $V = V_U + V_L$ is the total volume occupied by the phases in an apparatus; and F_U and F_L are the volumetric light and heavy phase flow rates, respectively.

Relying on the results [33], the set of Eqs. (1)–(8) was solved as follows.

First Cycle: Process Starts from the Motion of the Light Phase

Stage of light-phase motion

$$\frac{x(t_s, k)}{\bar{x}} = \frac{1}{t_s}\left[1 - e^{-at_s}\sum_{0}^{k}\frac{(at_s)^k}{k!}\right], \quad (9)$$

$$X_1(t) = \frac{x_1(t, n)}{\bar{x}} = e^{-a(t-t_s)}\sum_{0}^{n}\frac{[a(t-t_s)]^{n-i}}{(n-i)!}\frac{x(t_s, i)}{\bar{x}}, \quad (10)$$

$$X_1(k, t_{1U}) = \frac{x_1(k, \tau_{1U})}{\bar{x}} = e^{-a(t_{1U}-t_s)}\sum_{0}^{k}\frac{[a(t_{1U}-t_s)]^{k-i}}{(k-i)!}\frac{x(t_s, i)}{\bar{x}}. \quad (11)$$

Equation (9) describes the distribution of concentrations in a series of equilibrium cells (a column) at the end of the period of sample injection with the light-phase flow ($\tau = \tau_s$, $t = t_s$), and Eq. (11) describes the distribution of concentrations in this system at the end of the light- phase motion semiperiod ($\tau = \tau_{1U}$, $t = t_{U1}$). Equation (10) describes the output concentrations in the light phase (chromatogram).

Stage of heavy-phase motion

$$Y_1(k, t_{1L}) = \frac{y_1(k, t_{1L})}{\bar{x}} = K_D e^{-K_D a t_{1L}}\sum_{i=k}^{n}\frac{(K_D a t_{1L})^{i-k}}{(i-k)!}X_1(i, t_{1U}), \quad (12)$$

$$Y_1(t) = Y_1(0, t) = K_D e^{-K_D a t}\sum_{i=0}^{n}\frac{(K_D a t)^i}{i!}X_1(i, t_{1U}). \quad (13)$$

Equations (12) and (13) describe the distribution of concentrations in the system at the end of the heavy-phase motion semiperiod ($\tau = \tau_{1L}$, $t = t_{1L}$) and the output concentrations in the heavy phase (chromatogram).

Second and the Following Cycles

Stage of light-phase motion

$$X_j(t) = e^{-at}\sum_{i=0}^{n}\frac{(at)^{n-i}}{(n-i)!}X_{j-1}(i, t_{(j-1)L}), \quad (14)$$

where $t = (\tau F_U)/V$ and $t_{(j-1)L} = (\tau_{(j-1)L}F_L)/V$,

$$X_j(k, t_{jU}) = e^{-at_{jU}}\sum_{i=0}^{k}\frac{(at_{jU})^{k-i}}{(k-i)!}X_{j-1}(i, t_{(j-1)L}), \quad Y_j(k, t_{jU}) = K_D X_j(k, t_{jU}), \quad (15)$$

where j is the cycle number, $t_{jU} = (\tau_{jU}F_U)/V$ and τ_{jU} are the time of the stage of light-phase motion in the jth cycle in dimensionless and dimension time units.

Stage of heavy-phase motion

$$Y_j(t) = K_D e^{-K_D a t}\sum_{i=0}^{n}\frac{(K_D a t)^i}{i!}X_j(i, t_{jU}), \quad (16)$$

where $t = (\tau F_L)/V$.

$$Y_j(k, t_{jL}) = K_D e^{-K_D a t_{jL}}\sum_{i=k}^{n}\frac{(K_D a t_{jL})^{i-k}}{(i-k)!}X_j(i, t_{jU}), \quad (17)$$

$$X_j(k, t_{jL}) = \frac{Y_1(k, t_{jL})}{K_D}, \quad (18)$$

where $t_{jL} = \tau_{jL}F_L/V$ and τ_{jL} are the time of the stage of heavy-phase motion in the jth cycle in dimensionless and dimension time units.

It should be noted that Eqs. (9)–(18) were derived under the assumption that each stage of a cyclic process begins from the time moment $\tau = 0$. Moreover, the time of the light and heavy-phase motions was expressed in dimensionless units using the average residence time of a corresponding phase in a column.

The obtained dependences enable the modeling of the separation of a mixture of components in the countercurrent cyclic regime with a variable time of phase motion semiperiods under the conditions, when a sample is fed with one phase flow in the first cycle of the process for a certain time period (Fig. 1).

The numerical modeling results for the separation of a binary mixture ($K_{Da} = 0.5$ and $K_{Db} = 1.5$) in a column with a cell number $N = 100$ at a sample injection time $t_s = 0.1$ and $S = 0.5$ are shown in Fig. 2 as an example.

The above model contains many parameters, which allow us to determine the conditions and regime of the process for the separation of mixtures of different composition in extraction-chromatographic devices of various types. The particular role of the parameter t_s governing the efficiency of a separation process should also be emphasized. Thus, $t_s = 0.1$ in the example shown in Fig. 2. corresponds to a tenfold increase in productivity compared with the pulsed injection of a sample ($t_s = 0.01$).

To perform numerical studies and model the processes for separating the liquid mixtures based on the above dependences, we have developed a computer program. The program was created in the free Lazarus

environment in Object Pascal for the Free Pascal compiler. The Lazarus 2.6.2 version for Windows 32bit was applied. Lazarus was used under the terms and conditions of the GNU General Public License, and some libraries including LCL were used under the modified GNU Lesser General Public License giving the right to modify and distribute the initial code.

EXPERIMENTAL

Experiments were performed on the previously described unit with the pulsed injection of solvents [11, 23, 24]. Aspirin, caffeine, coumarin, salicylic acid, and their mixtures were used as a sample, and the two-phase hexane–methanol–ethylacetate–water system with a volumetric ratio of 1 : 1 : 1 : 1 was used as solvents. To provide the mutual saturation of the phases, they were carefully stirred by shaking in a separation funnel for 30 min before each experiment.

Experiments were performed at room temperature. A sample was injected at the beginning of a series of multicell columns (concurrently with the mobile phase flow). Detection was performed on a UVV 101.4 M spectrophotometer with a preparative cell installed at the outlet of the mobile phase from the unit at a wavelength of 270 nm.

Three series of experiments were performed, namely, the recording of chromatograms for individual components in a series of two multicell columns in the one-stage process with a mobile heavy phase and a mobile light phase and the separation of a mixture of components in a series of four multicell columns in the cyclic process.

RESULTS AND DISCUSSION

The experimental and calculated peaks of individual components for the one-stage process with a mobile heavy phase and a mobile light phase are shown in Figs. 3 and 4, respectively. The experiments in which the heavy phase was mobile, were performed on a series of four columns, and a series of two columns was used in the experiments, in which the light phase was mobile. The distribution coefficients K_D (as a ratio of the concentration in the mobile phase to the concentration in the stationary phase) and the number of equilibrium cells required for calculations were determined from experimental peaks. Calculation results can be stated to demonstrate acceptable agreement with experiment.

The experimental chromatogram obtained for an equiconcentration sample consisting of aspirin, caffeine, and coumarin in a series of four multicell columns in the one-stage process with a mobile heavy phase is shown in Fig. 5. As can be seen, the separation of components is not attained in this regime.

The experimental chromatograms obtained for an equiconcentration sample of salicylic acid, aspirin, and caffeine in a series of four columns in the process

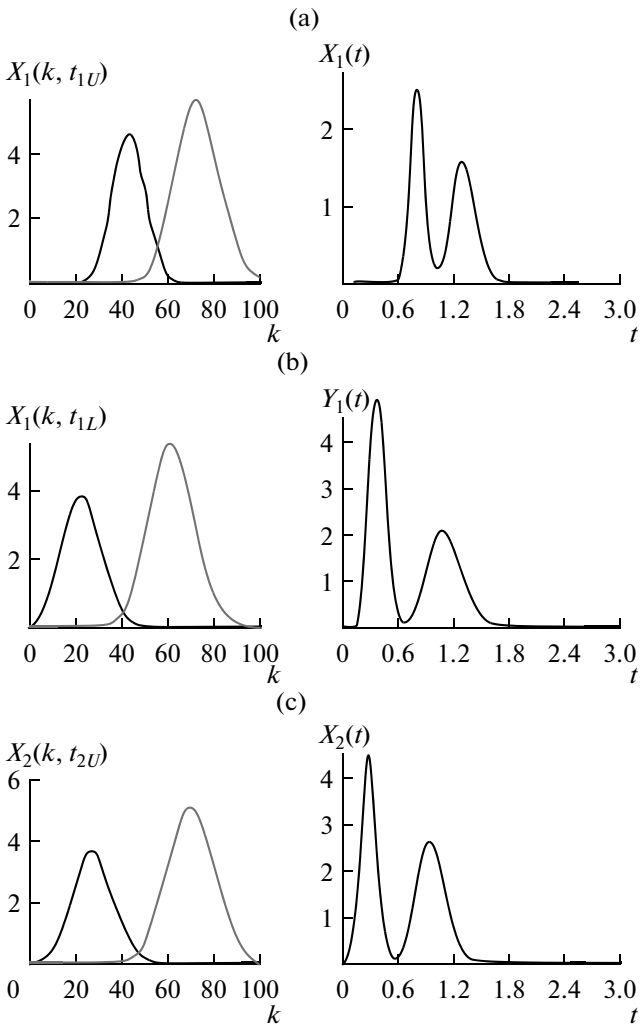

Fig. 2. Numerical modeling of the process for the separation of a binary mixture ($K_{Da} = 0.5$ and $K_{Db} = 1.5$) at process parameters $N = 100$, $S = 0.5$, $t_s = 0.1$: (a) first cycle, stage of light-phase motion, time $t_{1U} = 0.6$, (b) first cycle, stage of heavy-phase motion, time $t_{1L} = 0.18$, (c) second cycle, stage of light-phase motion, time $t_{2U} = 0.07$. Component concentration profiles in a column (in a set of cells) at the stage end are at the left, and output chromatograms for this process stage are at the right.

performed in two stages according to Fig. 1 are shown in Fig. 6. The complete separation of components is attained in this experiment: the salicylic acid peak came out with the mobile light phase at the first stage, and the caffeine and aspirin peaks came out with the mobile heavy phase at the second stage. The calculated chromatograms for this process are shown in Fig. 7. The calculation was performed using the data obtained in the experiments with individual components in the one-stage process with a mobile heavy phase and a mobile light phase. As can be seen from Figs. 6 and 7, the experimental and theoretical chromatograms are in good agreement with each other.

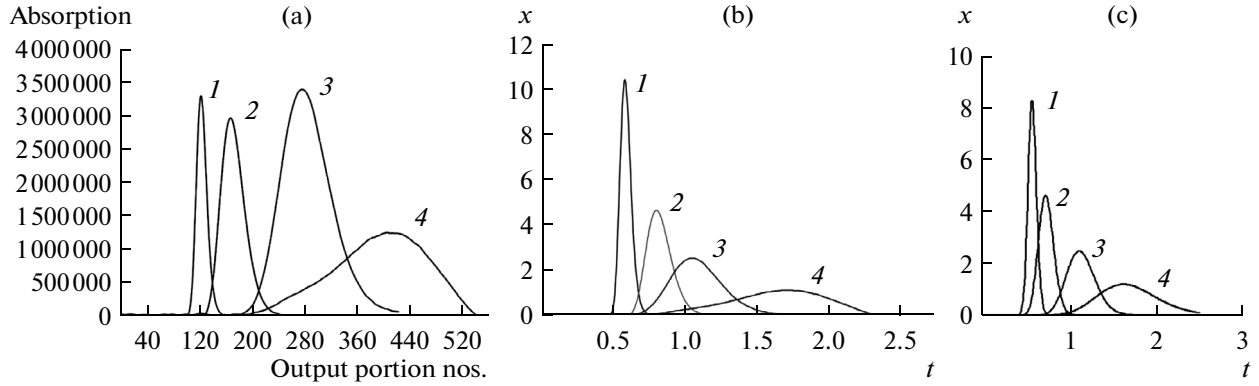

Fig. 3. Experimental (a) nonnormalized and (b) normalized and (c) calculated normalized peaks of individual components for the one-stage process with a mobile heavy phase in a series of four columns at $S = 0.4$–0.6: (*1*) caffeine, $K_D = 0.18$, $N = 150$, (*2*) aspirin, $K_D = 0.5$, $N = 76$, (*3*) coumarin, $K_D = 1.31$, $N = 51$, (*4*) salicylic acid, $K_D = 2.4$, $N = 26$.

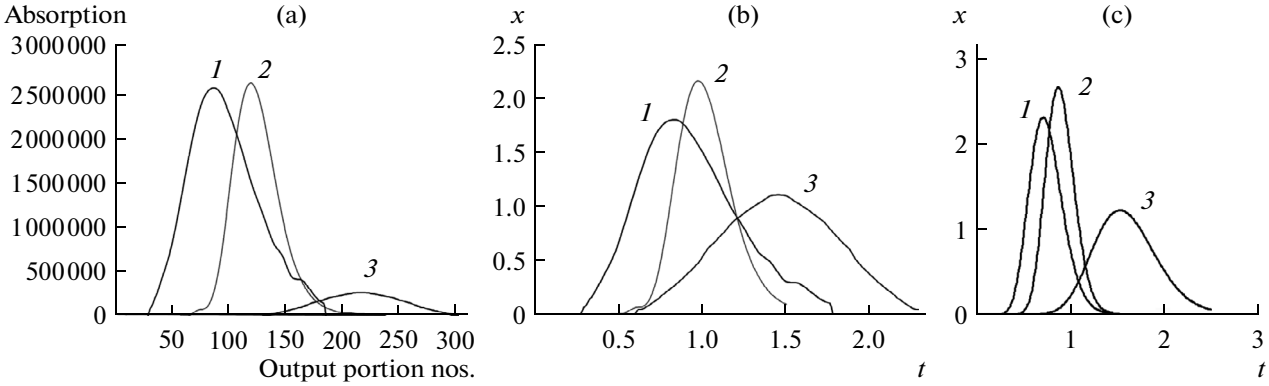

Fig. 4. Experimental (a) nonnormalized and (b) normalized and (c) calculated normalized peaks of individual components for the one-stage process with a mobile light phase in a series of two columns at $S = 0.4$–0.6: (*1*) salicylic acid, $K_D = 0.59$, $N = 39$, (*2*) coumarin, $K_D = 0.83$, $N = 35$, (*3*) aspirin, $K_D = 2.0$, $N = 23$.

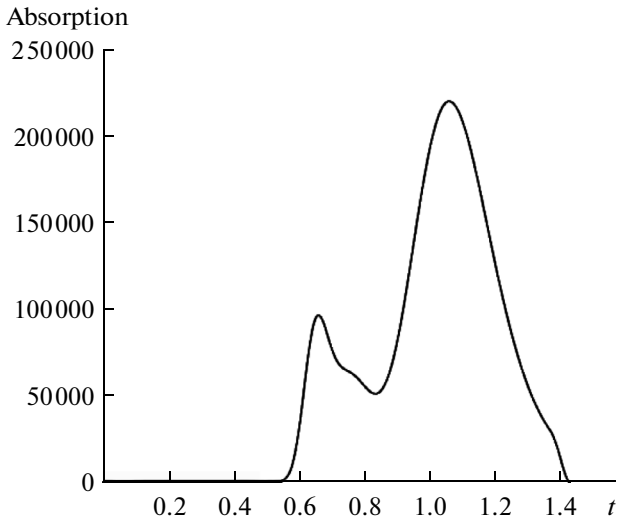

Fig. 5. Experimental chromatogram obtained for a sample consisting of aspirin, caffeine, and coumarin in a series of four multicell columns in the one-stage process with a mobile heavy phase.

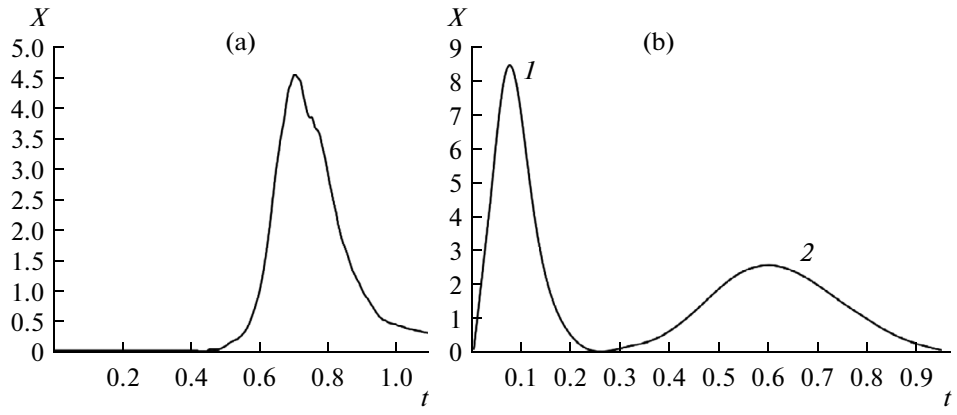

Fig. 6. Experimental chromatograms obtained for an equiconcentration sample consisting of salicylic acid, aspirin, and caffeine in a series of four columns in the two-stage process according to Fig. 1: (a) chromatogram of salicylic acid at the first stage (t_{1U} = 1.1), (b) chromatograms of (*1*) caffeine and (*2*) aspirin at the second stage.

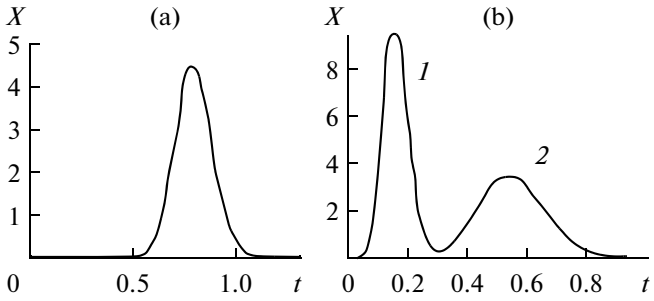

Fig. 7. Calculated chromatograms for the experiment illustrated in Fig. 6 at $S = 0.5$: (a) chromatogram of salicylic acid at the first stage, $N = 78$, $K_D = 0.59$, $t_{1U} = 1.1$, (b) chromatograms of (*1*) caffeine and (*2*) aspirin at the second stage, $N_1 = 100$, $K_{D1} = 7.0$, $N_2 = 60$, $K_{D2} = 2.0$.

CONCLUSIONS

A new method for the extraction separation of a mixture of components in the countercurrent cyclic regime with a variable phase motion semiperiods under the conditions, when a sample was injected with one phase flow for a certain time period in the first cycle of the process, was analyzed. The mathematical model of the process was developed, and some analytical relationships for the modeling and calculation of similar processes were derived.

The comparison of experiment and theory was performed, and satisfactory agreement between them was established. The prospects of the new method that provides a considerable increase in the efficiency of processes for the extraction separation of liquid mixtures was shown. The further development of this method as applied to the technology of rare-earth elements is planned. Intensified columns [34] can be used for its implementation on an industrial scale. To increase the efficiency of a dynamic (nonstationary) process, the batch injection of an initial solution into the system is proposed instead of its one-time injection considered in this work.

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