A new nonisothermal ion-exchange method for enrichment of solutions

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A new dual temperature ion-exchange method for concentration and separation of solutes, the "swinging wave" method, was described. The method can be used for the reactant-free enrichment of solutions in microcomponents. The effectiveness of the method applied to the enrichment of bromides in sea water on a highly basic anion-exchange resin was demonstrated, and technological characteristics of this process were studied using computer simulation and experimental studies.

Key words: ion exchange; dual temperature method; separation of components; computer simulation.

The development of the theory and practice of ion exchange is related to the creation of new, ecologically safe processes of separation and concentration of substances. Reactant-free processes performed through a directed change in the selectivity of ion exchangers by variation of the physical parameters, for example, temperature, are of special significance. The known dual temperature sorption methods based on the use of sorbents with temperature-controlled selectivity, *e.g.*, the "parametric pumping" method,[1,2] and the dual temperature countercurrent ion exchange[3] and its different analogs with a fixed ion-exchange bed,[4] have restrictions that decrease the efficiency of these methods. In particular, the most developed parametric pumping method can be used for the preparation of high-purity substances, but it is not appropriate for manyfold enrichment of solutions in a target component (TC), especially when the volumes of the solutions are great.[5] A solution can be substantially enriched by dynamic dual parametric methods such as the countercurrent ion exchange method and its analogs, since they make it possible to control the concentration profiles of components in sorption layers and to create narrow zones with "peak concentrations." These methods are basically restricted by the necessity of matching rigidly the physical velocities of the motion of the sorbent and solution or movement of the heating zones and solution with the physicochemical parameters of the sorbent. This leads to several problems: the necessity of external heating or cooling of columns, a low degree of heat recuperation, a low stability of the process with respect to variation of the parameters, *etc.*

Previously, the feasibility of a new dynamic method, the "swinging wave" method,[6] in which the processed solution plays the role of the heat carrier, has been theoretically shown. The problem of enrichment of the solution was considered in the simplest linear approximation. Several versions of the method have been developed to perform continuous enrichment processes[7] oriented to the concentration of bromine, potassium, and rare elements from complex solutions and natural water by cation- and anion-exchange resins.

In this work, we estimated quantitatively the efficiency of this method for real values of physical parameters, taking into account the nonlinear and nonequilibrium character of the processes, and the enrichment in sea water of bromides was experimentally and theoretically studied. The "swinging wave" method was shown to be a sufficiently efficient reactant-free method for the concentration and separation of substances.

Description of the method

The method is based on the effect of compression of the concentration wave on passing from the zone with a lower sorption capacity of a component to the zone with higher sorption capacity. This can be easily shown for the linear isotherm described by the equation

$$\mu_i = \Gamma_i(\theta) \cdot C_i, \qquad (1)$$

where $\mu_i(Z)$ is the equilibrium content of the ith component in the unity volume of the sorbent layer corresponding to the longitudinal coordinate in the column Z ($Z = 0$ is the inlet of the column, $Z = L$ is the outlet); Γ_i is the partition coefficient between the solution and sorbent; C_i is the concentration of the ith component in the solution, $\theta(Z, t)$ is the temperature of the sorbent, and t is time. In

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2166—2172, December, 1997.

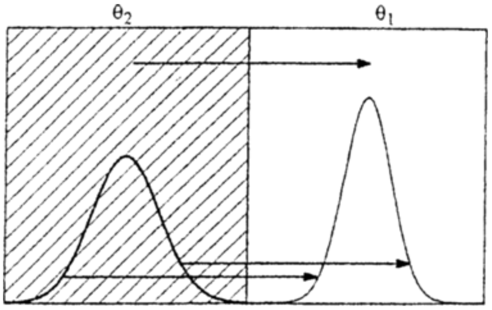

Fig. 1. Transfer of the concentration wave accompanied by "compression."

this case, the phase velocity of any point of the exchange front is determined by the correlation

$$v_i(\theta) = q/[\varepsilon + \Gamma_i(\theta)], \qquad (2)$$

where q is the linear velocity of the movement of the solution normalized to the cross section of the column and ε is the porosity of the sorbent layer. If $\Gamma(\theta_2) < \Gamma(\theta_1)$, $v(\theta_2) > v(\theta_1)$. The points of the trailing edge, as seen in Fig. 1, pass the major portion of the path at the temperature θ_2 with velocity $v_2 = v(\theta_2)$, while the points of the leading edge pass the major portion of the path at θ_1 with a lower velocity ($v_1 = v(\theta_1)$). A similar regularity, but described by more complicated correlations, is retained in the nonlinear case when the sorption isotherm of the target component is convex.

The simplest version of the "swinging wave" method can be realized on a setup consisting of two equivalent sorption columns (Fig. 2). Let us consider the case where the selectivity of the ion exchanger with respect to TC decreases as the temperature increases ($\Gamma(\theta)$ is a descending function).[8,9] Before the beginning of the process, the target component in the ion exchanger in both columns is in equilibrium with the original cool solution with temperature T_c ($T_c = \theta_c$ under equilibrium conditions). The overall concentration of TC in the column (in both the sorbent and solution) is equal to $m(0)$. Then the solution in one column is heated to the temperature T_h (for example, due to some external heat source), and the solution in the other column remains cool. This state will be considered to be the starting state of the system.

The process is performed in cycles. Each cycle includes three stages: the redistribution of TC, the change in temperature, and the sorption of TC from the original solution. At the beginning of each cycle, the system is in the starting state: the solution in the cool column has the temperature T_c, and the solution in the hot column has the temperature T_h ($T_h > T_c$). The heated region of the system is shaded in Fig. 2. Before some $(n + 1)$th cycle, the hot column *1* contains a certain amount of TC, which will be called the accumulation $m(n)$. At the beginning of the first cycle, the accumulation is equal to $m(0)$.

The cycle begins with the stage of redistribution of TC. The circular flow of the solution with the velocity q

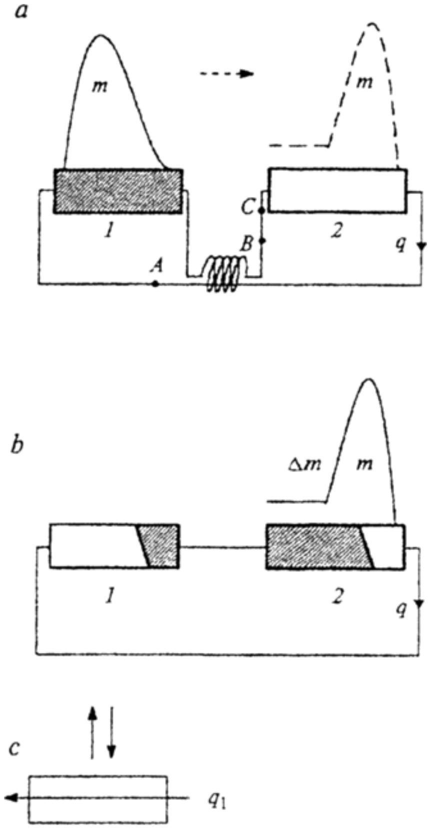

Fig. 2. Scheme of the work of the two-column setup for enrichment of solutions through the "swinging wave" method: transfer of the concentration wave of the target component from the heated column to the cooled column (*a*), change in temperatures in the columns by the circulating flow (*b*), and sorption of the target component from the original solution (*c*).

is created. At this stage, the temperature regimes in the columns should be steady-state but different from one another. The latter condition is fulfilled by the heat exchange between the equivalent counter flows in a countercurrent heat exchanger between sections. In an ideal adiabatic system, under the condition of local internal thermal equilibrium at each point of the heat exchanger, the temperatures in the columns would remain unchanged. In fact, some amount of heat is lost, which is compensated by additional heating and cooling in points *A* and *B*. The accumulation zone is transferred to the cool column *2* by the flow of the solution. The leading edge of the zone moves over the cool sorbent, and the trailing edge moves over the hot sorbent. Since, for the case where $\Gamma(\theta)$ is a descending function, according to Eqs. (1) and (2), the phase velocity of points of the concentration profile increases as the temperature increases, the mean velocity of the transfer of the leading edge is less than that of the trailing edge. As a result, the length of the accumulation zone decreases, and the concentration of TC in this zone increases. After the end of the first stage, the m "accumulation" is collected in the cool column *2*, and the remaining portion of this column contains some additional amount of TC.

The second stage of the cycle is the change in the temperature of the sections. The heat exchanger is switched off (see Fig. 2, *b*), and the circulating solution changes the temperature of the columns: column *2* containing the accumulation becomes hot, and column *1* becomes cool. When the column with the accumulation is heated, its $\Gamma(\theta)$ changes, and an additional amount of TC comes to the solution from the sorbent. As a result, after the first and second stages, the amount of TC in the solution in the heated column *2* increases by Δm compared to the beginning of the cycle, and in the cool column *1* it decreases by the same value. The cool column *1* becomes depleted.

The third stage is the co-feeding of the system from the external original solution. The heated section is switched off, and the original solution is passed through the cool depleted column *1* until equilibrium with respect to TC is established. This is the end of the cycle, and the system is considered to be brought to the state starting for the next cycle.

In the next cycle, the solution moves to the opposite direction, and the columns exchange their roles and temperature regimes. The *m* accumulation increases from cycle to cycle, and the accumulation zone (concentration wave) moves in an alternating direction, in each cycle going from the depleted hot column to the cool column, which is preliminarily brought to the state of equilibrium with the original solution. After the necessary degree of enrichment is achieved, the preparation part of the process is completed. In the working part, when the accumulation zone goes from column to column, the product is removed from the system at time intervals corresponding to the "passage" of the peak of the concentration wave of the component through the sampling point (*C*). The velocity of removal of the product and the regime of "co-feeding" with the original solution are chosen in such a way that the total volume of the system remains unchanged, and the parameters of the concentration wave of TC, which passes through the sampling point and changes its direction from cycle to cycle ("swinging" wave), remain unchanged.

The simplest version of the "swinging wave" method described above can be improved to arrange a continuous process of sorption of TC from the original solution.[7] For this purpose, the third column should be included in the system. When the stages of redistribution of TC and temperature are carried out in two columns, the sorption occurs in the third column. Then the positions of the third ("charged") and depleted columns are exchanged, and the next cycle begins.

Mathematical model

The process of the mass transfer and the movement of the temperature fronts in each column are considered in terms of the following model.

$$\varepsilon(\partial C_i/\partial t) + q(\partial C_i/\partial Z) + \partial a_i/\partial t = 0,$$
$$0 \le Z \le L,\ i = 1, 2, \qquad \text{(mass transfer)} \quad (3)$$

$$\partial a_i/\partial t = \beta(\mu_i - a_i),\ \beta = \beta(C, \theta),$$

$$C_1/\mu_1 = K(\theta) C_2/\mu_2,\ \sum_{i=1}^{2} a_i = A_\Sigma, \quad \text{(exchange equilibrium)} \quad (4)$$

$$\varepsilon(\partial T/\partial t) + q(\partial T/\partial Z) + \sigma(\partial\theta/\partial t) = 0,$$
$$\partial T/\partial t = \alpha(T - \theta). \qquad \text{(heat transfer)} \quad (5)$$

In these correlations, $a_i(Z,t)$ is the content of the component per unit volume of the sorbent layer, which depends on the longitudinal Z coordinate and time t ($t = 0$ corresponds to the beginning of the cycle); β is the effective mass-transfer coefficient; $K(\theta)$ is the selectivity coefficient of the ion exchanger; A_Σ is the total exchange capacity per unit volume of the sorbent layer; σ is the thermal conductivity coefficient of the sorbent phase normalized to the unit volume of the layer; and α is the kinetic heat-transfer coefficient in the sorbent.

The initial and boundary conditions for the concentrations of the components and the temperature of the two columns correspond to the description presented above.

To consider the particular problem of the extraction of Br^- from sea water, let us designate Cl^- and Br^- by indices 1 and 2, respectively. Note that Eq. (4) is a particular case of the mass action law for a two-component solution containing compounds of exchanging monocharged ions.

In the simulation of the process, it is interesting to study the dependence of the accumulation dynamics on the cycle duration and its stages. Therefore, the duration of each stage of the cycle was not fixed in the calculations; instead ending criteria were introduced: (1) for the first stage, the achievement of the accumulation maximum in the cool column; (2) for the second stage, the completion of the change in temperatures of the sections; and (3) for the third stage, the achievement of the specified level of filling the column with the component.

A differential scheme similar to that presented previously[10] was used to solve the system of equations (3)—(5).

Hereinafter, for simplicity, numerical values of magnitudes entering the equations of the model are given without dimensionalities. These magnitudes are measured in the following units: C, a, m, μ, and A_Σ in g-equiv. L^{-1}, t in h, Z in m, α and β in h^{-1}, q in m h^{-1}, σ in J L^{-1} deg^{-1}, and ε and K are dimensionless magnitudes.

Parameters of the model applied to the concentration of Br^- in sea water

The values of the parameters of the model were taken from the experimental data obtained previously for the ion exchange of Cl^- and Br^- on the highly basic AB-17 and Dowex-1 anion-exchange resins with tetraalkylammonium functional groups.[8] According to a detailed procedure,[8] a series of dynamic experiments on the frontal ion separation was performed: solutions of mixtures of salts containing Br^- and Cl^- ions in different concentrations were passed through ion-exchange columns with anion-exchange resins at temperatures of $T_c = 9$ °C and $T_h = 90$ °C, and the composition of eluted solutions was analyzed. Based on this analysis, the selectivity coefficients (equilibrium constants of ion exchange of chlorides and bromides) on different sorbents were determined at different concentrations of components and temperatures. Additional studies at intermediate values of temperatures were performed for the AB-17×8 anion-exchange resin. Experiments with real sea water containing sulfate ions along with bromides and chlorides were also carried out. It was established that SO_4^{2-} anions in concentrations corresponding to their content in sea water have almost no effect on the exchange of Br^- and Cl^-.

The results of the experiments can be briefly formulated as follows. 1. The equilibrium of the exchange of bromides and chlorides is described by Eqs. (4), from which the Langmuir isotherms for each of the components can be easily derived. The constant of exchange of Br^- by Cl^- is independent of the ratio of their concentrations in the original solutions when the overall concentration of salts (C_Σ) in these solutions is unchanged, and its temperature dependence has the form

$$K(\theta) = K_0 f(\theta), \tag{6}$$

$$\partial \ln K(\theta)/\partial\theta = \Delta H/(R\theta^2), \tag{7}$$

where K_0 is the exchange constant at the specified temperature θ_0, and $f(\theta) = \exp[-\Delta H/R\cdot(\theta^{-1} - \theta_0{}^{-1})]$ is the temperature function; ΔH (J mol^{-1}) is the change in the differential enthalpy during the transfer of one mole of the chloride form of the anion-exchange resin to the bromide form.

2. The exchange kinetics is described by an additive model for the mixed-diffusion process (for the following values of the parameters: $8\cdot10^{-4} \le C_2 \le 8\cdot10^{-2}$, $C_\Sigma = 0.5$, $r \approx 3.75\cdot10^{-4}$, $0.1 \le q \le 1$):

$$1/\beta = \Gamma/\beta^* + 1/\gamma, \tag{8}$$

where $\Gamma = \dfrac{KA_\Sigma/C_\Sigma}{1+(K-1)C_2/C_\Sigma}$,

$$\beta^* = \beta_0 q^{1/2} f'(\theta)/r^{3/2},\ \gamma = \pi^2 D_0 f''(\theta)/r^2, \tag{9}$$

$$\partial \ln f'/\partial\theta = \Delta E(\beta^*)/(R\theta^2), \tag{10}$$

$$\partial \ln f''/\partial\theta = \Delta E(\gamma)/(R\theta^2). \tag{11}$$

Here r is the average radius of grains of the ion-exchange resin (m); γ is the mass-transfer coefficient in the sorbent phase (h^{-1}); β^* is the external diffusion coefficient (h^{-1}); $\Delta E(\beta^*)$ is the activation energy of the interdiffusion of Br^- and Cl^- ions in the solution (J mol^{-1}); $\Delta E(\gamma)$ is the activation energy of the interdiffusion of Br^- and Cl^- ions in the ion exchanger phase (J mol^{-1}); D_0 is the coefficient of the particle diffusion of Br^- in the chloride form of the anion-exchange resin (m^2 h^{-1}); β_0 and γ_0 are the equilibrium and kinetic parameters (with accuracy up to numerical coefficients) at the specified temperature, at which the corresponding functions f' and f'' have unity values.

The following parameters of the model for the system of equations (3)—(11) were used in experiments with the AB-17×8 anion-exchange resin or determined by an independent method: $\varepsilon = 0.36$; $A_\Sigma = 1.43$; $C_1|_{(Z=0)} = 0.5$; $C_2|_{(Z=0)} = 8\cdot10^{-4}$; $K(\theta)|_{298K} = 4.3$; $\Delta H = -5.7\cdot10^3$; $\beta^*(298) \approx 140$ (at $q = 5$); $\gamma(298) = 25$; $D_0(298) = 3.2\cdot10^{-7}$; $\Delta E(\beta^*) \approx 8.3\cdot10^3$; $\Delta E(\gamma) = 16.9\cdot10^3$. A more detailed study of the kinetic processes will be published elsewhere.

It was established that the use of the equilibrium and kinetic parameters presented in the simulation of exchange processes in the Br^-—Cl^--anion-exchange resin systems by Eqs. (1)—(6) makes it possible to obtain results that agree well with experimental elution curves.

Results of simulation of enrichment by the "swinging wave" method

Figure 3 presents the $C_{max}(n)$ and $\Delta m(n)$ dependences for $q = 2$ and $q = 5$ when $L = 1$. These q values were chosen for demonstration because when $q = 2$ the enrichment process is highly efficient and degrees of

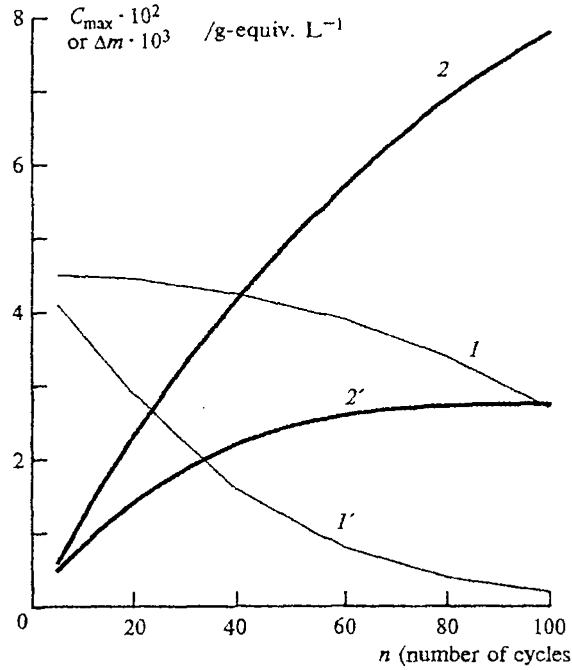

Fig. 3. Accumulation of the target component per cycle (Δm) (*1, 1′*) and its concentration in the peak (C_{max}) (*2, 2′*) at different numbers of the cycle, at $q = 2$ (*1, 2*) and 5 m h^{-1} (*1′, 2′*).

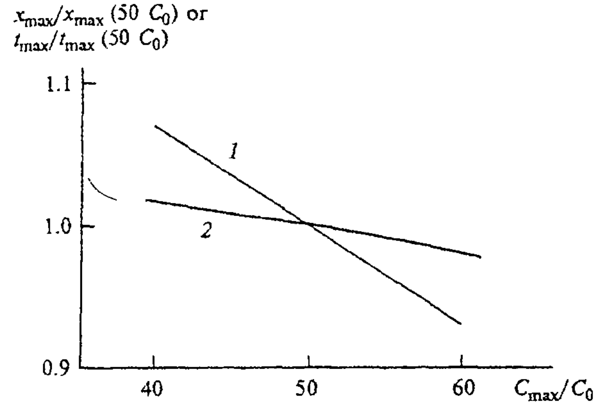

Fig. 4. Distance covered by the peak (x_{max}) (*1*) and optimum moment of removal of the product (t_{max}) (*2*) at different concentrations in the peak. Curves are normalized to the average value.

enrichment of the solution up to 150 times can be achieved, while $q = 5$ corresponds to a sufficiently high velocity of the movement of the solution.

The optimum moment of removing products from the system, which coincides with the moment of the elution of the concentration peak of the target component from the column (t_{max}), and the distance covered by this peak in the column (x_{max}) depend on the value C_{max}. The $t_{max}(C_{max})$ and $x_{max}(C_{max})$ dependences normalized to $t_{max}(50C_0)$ and $x_{max}(50C_0)$, respectively, for $q = 2$ are presented in Fig. 4. These data demonstrate variations of the distance covered by the concentration peak over a cycle and of the time of the optimum elution of the product as the degree of enrichment of the solution changes. When C_{max} varies from $40C_0$ to $60C_0$, the distance covered by the peak changes by 14% and the time changes by only 4%. The stability of the moment of elution of the product is supported by the alternating direction of movement of the solution in the column. In the technological regime, this stability makes it possible not to change the moment of product removal when C_{max} is varied, unlike, *e.g.*, the process that occurs *via* the circular column scheme.[4]

Optimization of the process through the amount of the product removed in the steady-state regime is one of the most important problems that can be solved by simulation. The steady-state regime occurs when $\Delta m = 0$ and is determined by values of the parameter q, the concentration of TC in the eluate (C_{end}), and the amount of TC removed per cycle ($\Delta\tilde{m}$). We shall call the amount of TC removed per unit time, $E^* = \Delta\tilde{m}/\Delta t$, the efficiency of the process. $E^* = E^*(C_{end}, q)$.

Let us examine the dependence of the effectiveness on q with fixed C_{end}. For this purpose, one should determine the steady-state regime of the process, at which the maximum amount of the substance per unit time is removed, and the concentration of the solution should be not less than the specified value. The results of optimization of the efficiency of the process (E^*) for $C_{end} = 10C_0$ and $C_{end} = 50C_0$ are presented in Fig. 5. The maximum E^* values for the C_{end} considered are observed at $q = 4.2$ and $q = 2.3$, respectively (when $L = 1$). When the flow rate increases, the E^* value decreases compared to the optimum efficiency due to smearing of the concentration peak and the corresponding decrease in $\Delta\tilde{m}$. When q decreases, the time of the cycle increases and, hence, $\Delta\tilde{m}/\Delta t$ decreases. The optimum q value is well pronounced, since the peak is less blurred.

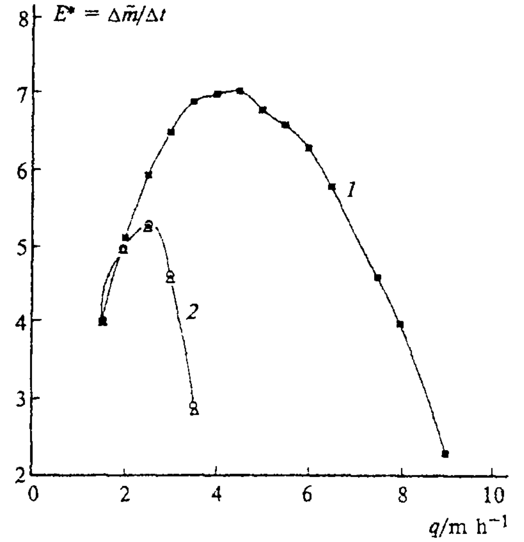

Fig. 5. Dependence of the efficiency of the process on the flow rate of the solution when the solution is enriched by 10 (*1*) and 50 times (*2*).

Comparison of experimental and calculated data

For experimental verification of the "swinging wave" method, bromide ions were concentrated in a model solution modeling sea water with the use of the AB-17×8 ion-exchange resin with the parameters presented above.

The three-column version of the "swinging wave" method described above was used. In this version, the first and second stages are performed in parallel with the third stage. Each column contained 15 mL of the sorbent, and the column length was 0.2 m. The process was performed at the following temperatures in the columns: $T_c = 3$ °C, $T_h = 78$ °C. The relative velocity of the solution flow was maintained to be $q/L = 2.6$ h^{-1}. The starting concentrations of components in the model solution, which was used as the original and circulating solutions, were $C_{Br} = 8 \cdot 10^{-4}$ and $C_{Cl} = 0.5$ g-equiv. L^{-1}. Laboratory experiments were carried out under isothermal conditions in each column. This is related to the fact that the complete adiabatic process of the "swinging wave" cannot be scaled to sizes less than some critical size, because the efficient work of a heat exchanger requires relatively large linear

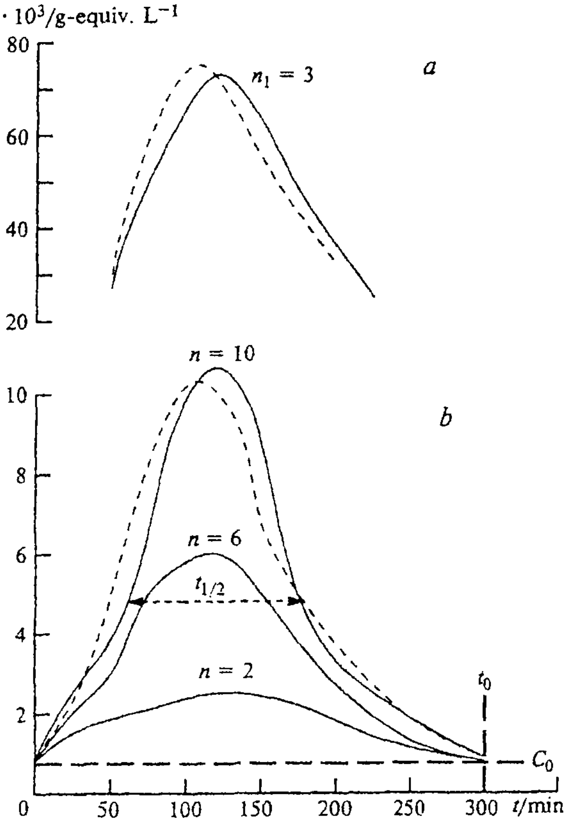

Fig. 6. Experimental (solid lines) and calculated (dotted lines) concentration profiles in the cyclic concentration of Br$^-$ in the solution modeling sea water: *a*. Before the process, one of the three columns was brought to equilibrium with the solution enriched by 50 times. *b*. In all columns, the anion-exchange resin was taken in the original Cl$^-$ form.

flows of the solution. Capillary effects and relative heat losses become noticeable when the sizes of the system are small. Nevertheless, as the results of the simulation show, in the process considered, the phase velocities of temperature waves are always higher than the phase velocities of concentration waves, and the isothermal version of the column simulates the actual process well.

Two series of experiments were performed. In the first series, the enrichment in Br$^-$ of modeling sea water was carried out beginning from the starting concentrations. This experiment corresponds to the region of Br$^-$ concentrations in solutions and ion-exchange resins with equilibrium described by the linear function (1). In the second series of experiments, one column was preliminarily brought to equilibrium with the solution: C_{Br} = $4 \cdot 10^{-2}$, C_{Cl} = 0.46 g-equiv. L^{-1}. After two starting cycles, the system entered the regime of the TC concentration by the "swinging wave" method.

The concentration profiles and results of simulation for both experimental series are presented in Fig. 6. The numbers of the cycles n correspond to the first series, and the number n_1 = 3 corresponds to the second series. Experimental profiles are drawn by solid lines, and the results of the simulation are shown by dotted lines.

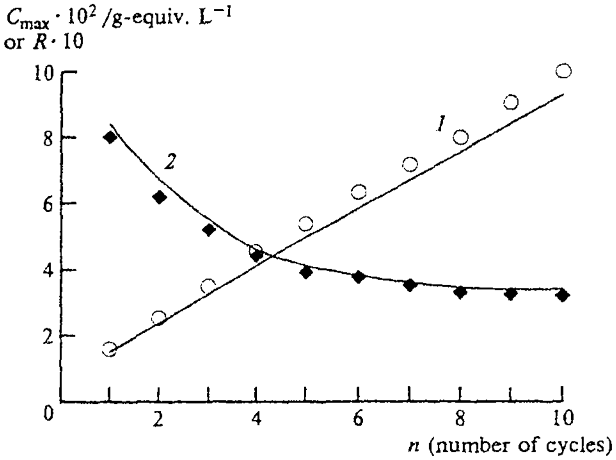

Fig. 7. Dependences of the concentration of Br$^-$ in the peak (*1*) and relative width of the peaks (*2*) on the number of cycles. Curves are the result of simulation, points are experimental data.

Let us consider the relative width of the concentration profiles $R = t_{1/2}/t_0$. The change in the C_{max} and R values from cycle to cycle is shown in Fig. 7. In the second series, R = 0.54 at n_1 = 3, which also agrees well with the results of the simulation.

The results obtained confirm that the model is valid and the dual temperature method proposed for the concentration of bromides is efficient. Estimation of some technological parameters of the concentration of bromides from sea water shows that the efficiency of the pilot plant with loading of 1 ton of the sorbent can produce a concentrate containing 1.2 ton Br$^-$ per year. The energy consumption is 10^8 kJ with heat losses of ~15%. The method proposed can be effectively used for the development of reactant-free and ecologically pure processes of concentration of different components from natural water. The method even needs no thermal treatment of the original water. In fact, according to the description presented above, the transfer of the concentration wave from the hot column to the cool column is performed by the same circulating solution. Contact with the external solution occurs only at the stage of co-feeding, which is carried out at a reduced temperature if $\Gamma(\theta)$ is a descending function. Therefore, a sorbent with a negative temperature coefficient of selectivity with respect to the target component should be chosen, for example, such as the highly basic AB-17 anion-exchange resin, which was used in the experiments on the concentration of bromides from the modeling sea water.

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Received January 10, 1997;
in revised form May 23, 1997