The Parametric Pump Mechanism in Separation of Components in Heterogeneous Systems. I. Macroscopic Distributed Systems

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Abstract. A dynamic method is proposed for the separation of the electrolyte components using a parametric pump with an ion exchange column It was studied experimentally and described mathematically The parametric separation of mixtures is based on interactions of two oscillating fields with a heterogeneous system containing two phases, a liquid and a solid one, the components of the mixture being able to redistribute between the phases The field of mechanical force is responsible for cyclic relative displacement of the phases, and synchronously changing temperature causes redistribution of the components between them This results in sodium and potassium fluxes opposite in direction which in turn leads to accumulation of sodium and potassium in opposite end cells

Key words: Ion exchange — Parametric pump — Fractionation

Introduction

New results in the field of dynamic systems theory, especially those concerning phenomena of spatio-temporal self-organization, generation of dissipative structures, auto-oscillations (Pavlasek 1998) and auto-waves in active media (Kadantsev et al 1997) revived the authors' interest in the parametric pump (PP) principle of mixture separation Separation methods based on the above principle are a part of dynamic chromatography and suggest periodic relative displacement of a het erogeneous system phases coupled to a changing external field, the field inducing changes in the distribution of the components between the phases

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The PP prıncıple was put forward by Wılhelm (1966), who was able to demon-strate ıts effectıveness by separatıon of the toluene/benzene mıxture wıth the sep-aratıon factor more than 10^6 (Wılhelm 1966, Wılhelm et al 1968) Later on, he as well as two of us (V A T and L V Y) used thıs prıncıple as the basıs for the con-structıon of a macroscopıc model of the cell membrane ıon channels (Wılhelm 1966, Tverdıslov et al 1973, Tverdıslov and Yakovenko 1980, Tverdıslov et al 1987)

We suggest that the PP mechanısm can be expected to be responsıble for redıstrıbutıon of components ın varıous bıologıcal and ecologıcal systems whıch subject to omnıpresent oscıllatıng (or fluctuatıng) external fields The processes ın the PP are quıte general and have very much ın common wıth the separatıon of components ın the lıvıng cell, soıl, the thın surface layer of natural water reservoırs, etc

The first part of thıs paper deals wıth experımental and theoretıcal study of macroscopıc systems whıle ın the second one we consıder possıble applıcatıons of the PP mechanısm to the molecular model of the cell membrane Na-pump

The parametrıc pump prıncıple

The most sımplıfied PP consısts of a two-phase system whıch ıs under the effect of two coherently oscıllatıng fields We studıed a system composed of two phases aqueous solutıon of sodıum chlorıde and potassıum chlorıde as a lıquıd phase and catıon exchange resın beads or a membrane as a solıd one The solutıon components to be separated ın our case are the catıons They are able to redıstrıbute between the phases One oscıllatıng field causes dısplacement of lıquıd phase components relatıve to the solıd phase, ı e ıt must provıde for a drıvıng force for the movement of ıons whıch are to be separated In dıfferent sets we used eıther mechanıcal force to dısplace the solutıon as a whole or electrıc field to only dısplace the ıons The second field was to govern the dıstrıbutıon of ıons between the phases by changıng the ıon exchange equılıbrıum constant In most experıments we used temperature for the purpose but pH was also successfully used ın a few sets The two oscıllatıng fields must be coherent After a few cycles ıt was possıble to observe non-zero tıme-averaged fluxes of sodıum and potassıum ın opposıte dırectıons

Materials and Methods

Two varıants of PP wıth temperature modulatıon were realızed The first one ıs shown ın Fıg 1 It consısted of an ıon exchange column wıth a thermostatıc water jacket The ınner dıameter of the column was 0 8 cm and ıts length was 60 cm The temperature of water ın the thermostatıc jacket was perıodıcally changed from 12 ± 1 to 80 ± 1 °C Each end of the column was connected to a receptacle, called the end cell, wıth a volume of 120 cm^3 ın whıch the solutıon was ıntensely stırred The two end cells were connected to a recıprocal pump that provıded for the perıodıc
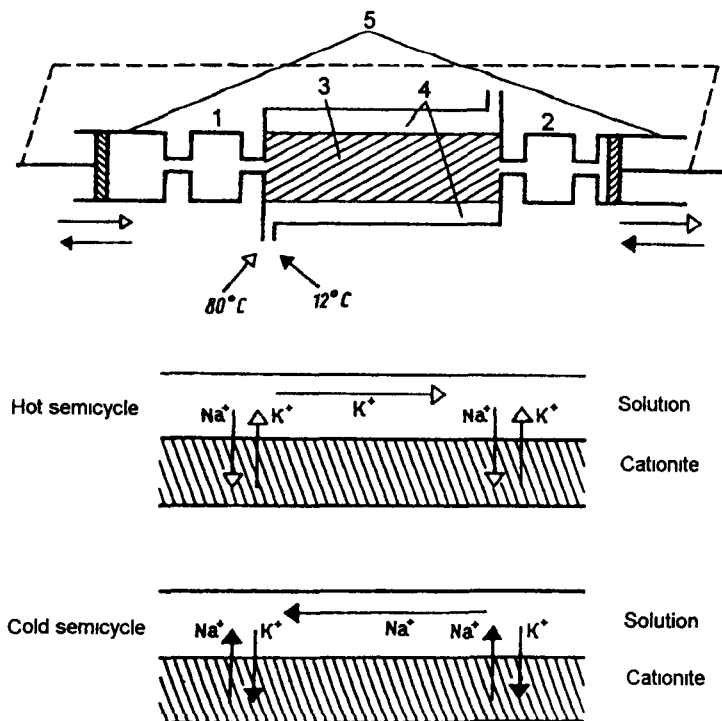
Figure 1. Schematic diagram of the parametric pump in which an ion exchange column is used for separation of cations 1, 2 – end cells, 3 – ion exchange column, 4 – thermostated water-jacket, 5 – the pump that provides back and forth movement of the solution in the column

back and forth flow of the electrolyte through the cells and the column. The total volume of the column was 30 cm^3, the volume of the solution in the column was 5–6 cm^3, the remainder being filled with the ion exchanger (or ionex). The volume of the solution pumped through the cells and the column during each half-cycle in different experiments was set at values such that the magnitude of the solution displacement in the column be between 3 and 33 cm. The cycle was usually set to 1000 s.

Changes of temperature and movements of the electrolyte were coherent. Fig. 2a shows the temperature changes in the center of the column as registered by a semiconductor microthermoresistor. Changes of average velocity of the solution in the column are also shown in the same Figure.

Before each experiment the ion exchanger was brought to equilibrium with an electrolyte solution containing 2.0 mmol/l NaCl and 2.5 mmol/l KCl. As the ion
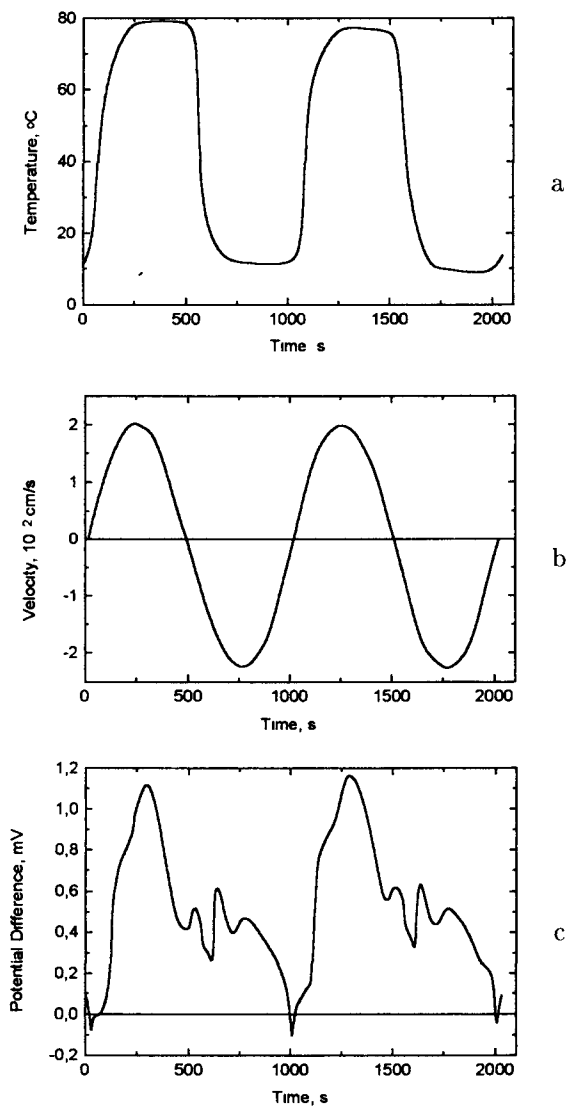
Figure 2. Changes of temperature (*a*) and velocity of the solution (*b*) at a poınt on the column's axıs, and electrostatıc potentıal dıfference between the end cells (*c*) for the desıgn shown ın Fıg 1 durıng 10-th and 11-th cycles of the pump

exchanger we used cationic ion exchange resin KU-2 (Reachim, Moscow). The practical specific capacity of the resin was measured by means of conventional static and

dynamic procedures (Helferich 1959; Tremillon 1965), and it was 4.9 ± 0.1 mmol H^+/g of dry exchanger at 20 °C. The concentration of fixed negative charges (sulfate groups in this case) in swollen resin beads was 1.5 ± 0.1 mmol/cm^3. The beads were of 0.5–1.3 mm in size.

The selectivity of an ionex is characterized by the ion exchange constant, $K_{K/Na}$ in our case:

$$K_{K/Na} = \frac{[K]^R \cdot [Na]^S}{[K]^S \cdot [Na]^R} \tag{1}$$

where [K] and [Na] stand for potassium and sodium ion concentrations, respectively, and the indices R and S stand for resin and solution respectively. This constant is also called fractionation coefficient.

The fractionation coefficient was measured with the use of both static and dynamic techniques (Helferich 1959; Tremillon 1965). The values obtained are given in Table 1.

Table 1 Fractionation coefficients as measured by static and dynamic techniques according to Helferich 1959 and Tremillon 1965

Temperature	12 °C	80 °C
Static $K_{K/Na}$	1 5	1 1
Dynamic $K_{K/Na}$	2 6	1 4

These data show that the affinity of the cationite (or catex) to potassium is always higher than that to sodium but the fractionation coefficients decrease 1.4–1.9 times with the increasing temperature.

In the other variant of the experimental setup the column was not thermostated. Instead, the two cells were kept at constant temperatures, one at 12 °C and the other one at 80 °C. In the column a temperature profile was formed and periodically disturbed as the solution moved from the cold cell to the hot one or in the opposite direction. The displacement magnitude in this setup was ca 3 cm.

Sodium and potassium chloride was from Reachim (Moscow, USSR). The concentrations of sodium and potassium ions were measured with the help of a PF-1 flame photometer (USSR).

Results and Discussion

In experiments with the periodically changing temperature potassium ions were found to accumulate in the cell (#2) into which the solution was delivered during the "hot" half-period, while sodium ions accumulated in the other cell (#1). After a sufficient number of cycles a steady-state asymmetric distribution of the ions was achieved. An electric potential difference was observed between the cells, cell #2 being negative.

The asymmetry of the ion distribution was characterized by the separation factor α:

$$\alpha = \frac{[K]^{S(2)} \cdot [Na]^{S(1)}}{[K]^{S(1)} \cdot [Na]^{S(2)}} \tag{2}$$

The separation factor increased as the magnitude of the solution displacement decreased. Its averaged (over 5 measurements for each set) and rounded values after 1000 cycles and different displacement magnitudes are given in Table 2. When the end cells were kept at different temperatures the separation factor was smaller: after 1000 cycles with 3 cm displacement magnitude it reached a steady-state value of about 2.

Table 2. Values of the separation factor for different displacement magnitudes

Magnitude of displacement, cm	30	15	3
α	3	8	50

The spatial separation of the sodium and potassium ions is accounted for by the fact that, at high temperatures the selectivity of the catex (i.e. the fractionation coefficient) decreases, and bound potassium ions are exchanged for free sodium ions. Therefore the solution during the "hot" half-period becomes enriched with potassium ions, and it is brought to cell #2. During the "cold" half-period all processes change their directions and the solution moves to cell #1. The reciprocal dependence of the separation factor on the magnitude of the solution displacement is usual for dynamic chromatography, and is explained by an increase of the number of theoretical equivalent dishes in the column. The cyclic changes of the electric potential difference between the cells look quite strange, and demonstrate the complexity of ion exchange processes in a column with moving electrolyte and changing temperature. The lack of symmetry between the half-periods of the electric potential changes may be explained by changes of the ion exchange velocity

with temperature, changes of temperature and ion concentration differences between the cells

In another experimental setup pH was used as the governing factor instead of temperature there was a pH difference of 1 to 6 between the initial solutions in the end cells Potassium ions were accumulated in the cell with lower pH The separation factor in this case never exceeded 3 Of course, any other third cation could have been used and this would have affected the ion exchange constant These issues exceed the scope of the present paper

One more experimental setup may be mentioned here which was also used but was not investigated in detail In this case, the PP consisted of ion exchange membrane separating two cells with the same electrolyte solutions but with different pH The fractionation coefficient of the membrane was about 2 Displacement of the ions in the membrane was achieved by means of an electric potential difference between the cells The separation factor in all experiments was not higher than 2

The theory of parametric pumping

Mathematical formulation of the PP model

The main principle of the PP is similar to the operation principle of synchronous demodulation Our treatment of the problem is based on the conventional approach to dynamic chromatography, i e on the use of the theoretical plates (TP) technique which allows for representation of dynamic process of ion exchange as a set of reactions at equilibrium, the system with distributed parameters being replaced by a discrete set of subsystems with constant parameters

We also assume that

1 The cycle duration is much longer than the ion exchange time constant (we do not consider any kinetics)

2 The time necessary for the selectivity constant $K_{K/Na}$ triggering from K_1 to K_2 is negligible

3 The solution displacement magnitude is exactly equal to the height of one TP

4 The ion concentrations are uniform inside each of the TP, changing step-wise at its boundaries

5 Diffusion and inhomogeneities of the solution flux in the column may be neglected

6 The specific capacity of the ionex is constant

The PP column may be represented as a series of n TP with the plate height l_0 Volume V_i of the solution displaced during each stroke of the pump is equal to the free volume of the TP, the solution being in contact with the initial TP's ionex during the first and fourth quarters of the period, and with the ionex of the neighboring TP during the second and third quarters It is supposed that the corresponding equilibrium states are reached instantly

Let us consider the equilibria in $(i-1)$-th and i-th TPs. Under equilibrium the solution in i-th TP has a composition determined by the equilibrium constant K_2. Then it is brought in contact with the ionex in $(i-1)$-th TP and the equilibrium constant is changed to K_1. After redistribution of ions between the solution and the ionex the solution is moved back into i-th TP, and, the equilibrium constant being changed to K_2 again, a new equilibrium is established. If the PP has reached a stationary state, the solution contents must be the same as prior to the first step in the cycle described.

Using the mass action law we obtain:

$$\frac{[K]^{R(i)}}{[Na]^{R(i)}} = K_2 \cdot \frac{[K]^{S(i)}}{[Na]^{S(i)}}$$

$$\frac{[K]^{R(i-1)}}{[Na]^{R(i-1)}} = K_1 \cdot \frac{[K]^{S(i-1)}}{[Na]^{S(i-1)}} \tag{3}$$

where $[K]^{R(i)}$, $[Na]^{R(i)}$, $[K]^{R(i-1)}$, $[Na]^{R(i-1)}$ are cation concentrations in the ionex and the solution in i-th and $(i$-1)-th TPs correspondingly.

Therefore,

$$\frac{[K]^{R(i)} \cdot [Na]^{R(i-1)}}{[Na]^{R(i)} \cdot [K]^{R(i-1)}} = \frac{K_2}{K_1} \tag{4}$$

Analogically, the ionex of $(i-1)$-th TP in two consecutive half-periods must be in equilibrium with the solution of i-th TP at K_1 and with the solution of $(i-1)$-th TP at K_2. Then

$$\frac{[K]^{S(i)} \cdot [Na]^{S(i-1)}}{[Na]^{S(i)} \cdot [K]^{S(i-1)}} = \frac{K_2}{K_1} \tag{5}$$

As such equilibria must hold for each pair of neighboring TPs we obtain for n TP

$$\frac{[K]^{R(n)} \cdot [Na]^{R(1)}}{[Na]^{R(n)} \cdot [K]^{R(1)}} = \left(\frac{K_2}{K_1}\right)^n \tag{6}$$

$$\frac{[K]^{S(n)} \cdot [Na]^{S(1)}}{[Na]^{S(n)} \cdot [K]^{S(1)}} = \left(\frac{K_2}{K_1}\right)^n \tag{7}$$

The latter equation coincides with the definition of the separation factor α. Therefore, the ultimate separation factor for ions in a parametric pump with a column containing n TPs and at displacement magnitude equal to the height of a single TP is:

$$\alpha = \left(\frac{K_2}{K_1}\right)^n$$

It is clear that the lower the displacement magnitude, the higher the separation factor. At the magnitude equal to the column length, $\alpha = K_2/K_1 \approx K_{K/Na}$(the second approximate equivalence holds when the ionex loses its selectivity at high temperatures). Of course, diffusion, convection and non-uniform speed of the solution flow in a real system decrease the separation factor. Besides, there are constructive limitations for such parameters as the displacement magnitude etc.

With this approach it is possible to show that the separation factor for ions in a PP with temperature or pH gradient is roughly equal to the selectivity coefficient of the ionex used.

Calculation experiment

The numerical experiment makes complete use of the discrete model of the PP. The possible non-equilibrium states of TPs are taken into account in the form of the mass action law:

$$[K^*]^{S(\imath)} + \nu[K^*]^{R(\imath)} = [K]^{S(\imath)} + \nu[K]^{R(\imath)}$$
$$[Na^*]^{S(\imath)} + \nu[Na^*]^{R(\imath)} = [Na]^{S(\imath)} + \nu[Na]^{R(\imath)},$$

where ν is the ratio of the ionex and the solution volumes, and the asterisk indicates non-equilibrium concentrations.

If the dependence of the ionex specific capacity on temperature may be neglected then total ion concentrations in the solution and in the ionex are constants, C^S and C^R, resp.:

$$[K^*]^{S(\imath)} + [Na^*]^{S(\imath)} = [K]^{S(\imath)} + [Na]^{S(\imath)} = C^S$$
$$[K^*]^{R(\imath)} + [Na^*]^{R(\imath)} = [K]^{R(\imath)} + [Na]^{R(\imath)} = C^R \qquad (8)$$

Besides, the mass action law gives:

$$\frac{[K]^{S(\imath)}}{[Na]^{S(\imath)}} = K_{K/Na}\,(T)\,\frac{[K]^{R(\imath)}}{[Na]^{R(\imath)}}, \qquad (9)$$

where $K_{K/Na}(T)$ is the ions fractionation coefficient at temperature T.

Substituting $[Na]^{S(\imath)} = C^S - [K]^{S(\imath)}$, $[Na]^{R(\imath)} = C^R - [K]^{R(\imath)}$ and $[K]^{R(\imath)} = ([K^*]^{S(\imath)} + \nu[K^*]^{R(\imath)} - [K]^{S(\imath)})/\nu$ into (9) we obtain:

$$A\left(\left[K^{S(\imath)}\right]\right)^2 + B[K]^{S(\imath)} - C = 0,$$

where:

$$A = 1 - K_{K/Na},$$
$$B = \nu C^R + K_{K/Na}C^S + (K_{K/Na} - 1)\left([K^*]^{S(\imath)} + \nu\,[K^*]^{R(\imath)}\right),$$
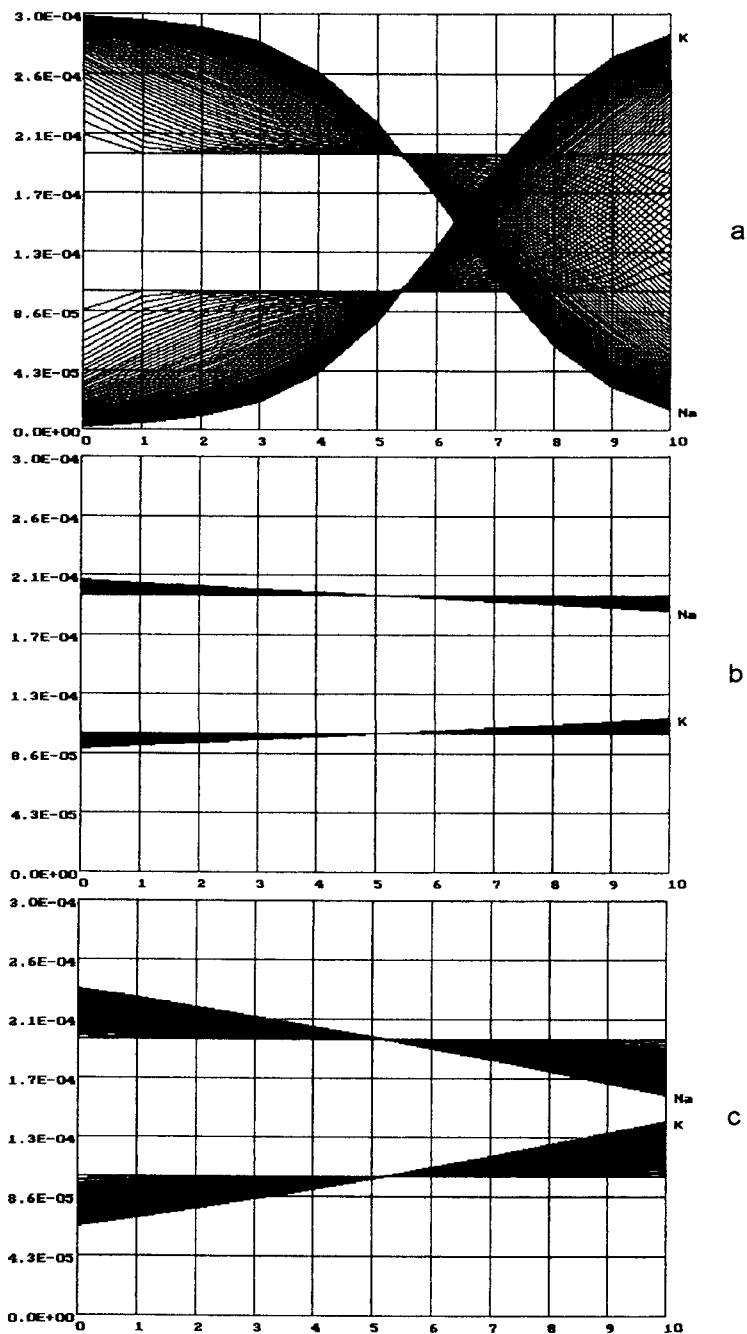$$C = K_{K/Na}C^S\left([K^*]^{S(\imath)} + \nu\,[K^*]^{R(\imath)}\right).$$

a

b

c

Figure 3. Time dependence of the concentration profiles in the column The x-axis shows the number of theoretical plates in the column, and the y-axis shows relative concentrations of sodium and potassium ions a) the profiles after $N = 107$ cycles, separation factor $\alpha = 2\ 979\ 10^3$, initial sodium and potassium concentrations were $1\ 0\ 10^{-4}$ and $2\ 0\ 10^{-4}$ relative units respectively, the catex non-dimensional specific capacity was $3\ 10^{-4}$, the ratio of the ionex volume to the volume of the solution, $\nu = 1\ 0$, the fractionation coefficients during hot and cold semi-cycles were $K_1 = 0\ 4$, $K_2 = 0\ 9$, the end cells' volumes and the solution displacement were equal to the volume of one TP, b) same conditions as in a) but $N = 178$, $K_1 = 0\ 87$, $K_2 = 0\ 9$, then $\alpha = 1\ 393$, c) same conditions as in a) but $N = 400$, $K_1 = 0\ 8$, $K_2 = 0\ 9$, then $\alpha = 3\ 247$

Once of this equation's roots is negative, therefore there is only one solution to it Upon solving this equation for each TP it is possible to obtain the potassium concentration profile and then, making use of (9), the sodium concentration profile in the column Figures 3 and 4 show the results of such calculations for a few sets of conditions

We would like to stress once more that the process of parametric separation of liquid mixture components may take place in numerous natural situations when oscillations are observed in heterogeneous systems So, in soil there are upward and downward directed fluxes of solutes synchronized with the soil temperature changes At the ocean-atmosphere boundary as well as at the littoral zone processes may be realized that result in parametric fractionation (Tverdislov and Yakovenko 1995) Ion pumps of cell membranes are, as a matter of fact, parametric pumps in which the affinity of specific groups to different ions is switched in the course of the energy donating chemical reaction of ATP hydrolysis (Tverdislov et al 1987) The parametric separation may turn to be very practical if used in fermentors built upon the principles of distributed active media

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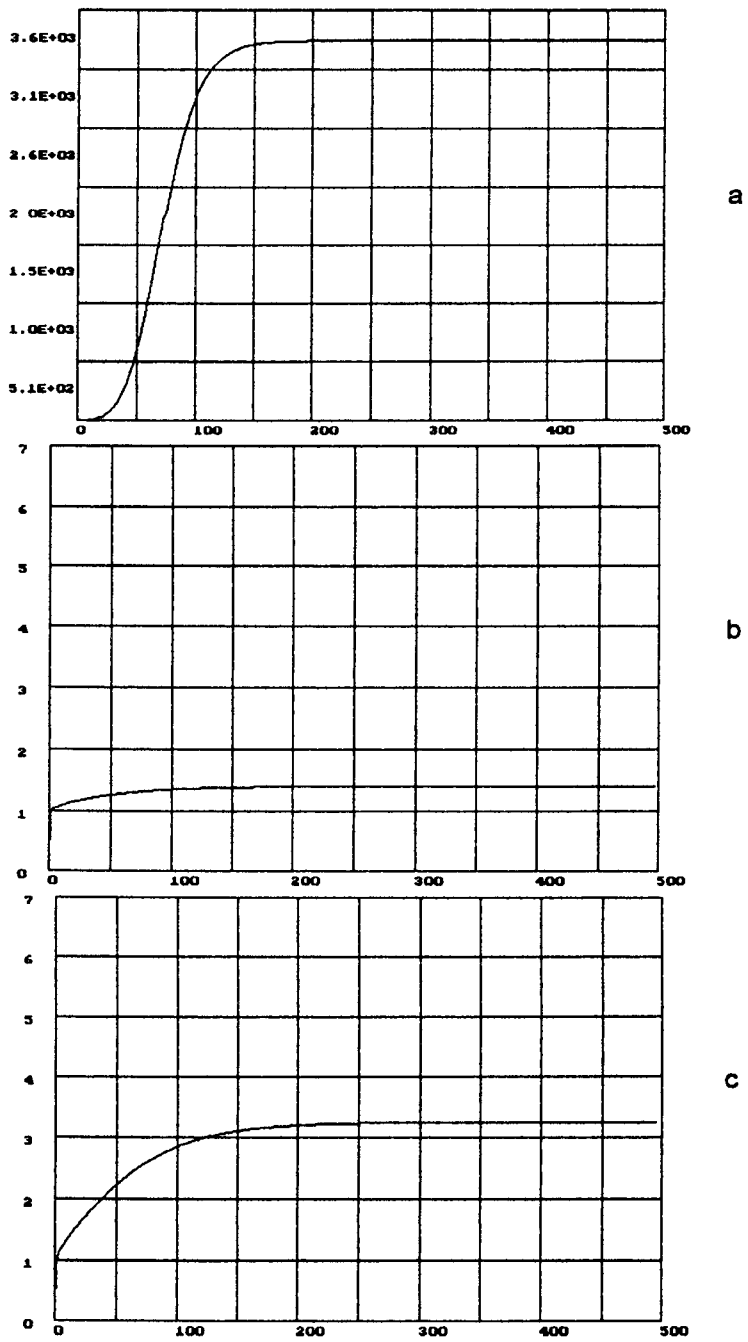Tremillon B (1965) Les Separations par les Resines Echangeuses d'Ions Gauthier-Villars, Paris

Figure 4. Tıme dependence of the sodıum to potassıum separatıon factor for the end cells (number of cycles), for all other condıtıons see Fıg 3

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