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SEPARATION BY ION EXCHANGE AND ADSORPTION PARAMETRIC PUMPING IV.

Theoretical Cycle, Number of Theoretical Cycles for Batch, Thermal Ion Exchange Parametric Pumping

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The best component separation can be achieved by the application of theoretical cycles. A local equilibrium analysis is provided, which gives, ideal efficiencies through either graphical or numerical calculations. As the calculations presented here ignore non-equilibrium ion exchange, the mixing phenomena and the "run out" of characteristics, they are significant mainly in relation to one another. Nevertheless, the effects of process and operation variables found here should be valid for actual system, especially in the production of high purity materials.

Introduction

The so-called equilibrium theories or models are the simplest variants of the theoretical analysis and mathematical modelling of parametric pumping processes. There are two determining theories in literature dealing with this subject. The first assumes continuous flow and column and uses the basic equation of chromatography for the mathematical description of the operation. By the second theory the column is separated to parts, to well mixed cascades and also the flow is discontinuous. For the mathematical description of the cyclic operation, the equilibrium cascade model is applied, this, regarding the computation technique, can easily be treated.

The first mathematical description of parametric pumping was given by WILHELM and co-workers [1], together with the basic idea of a new component separation moreover, the first experimental data were published. PIGFORD and co-workers [2] elaborated the chromatographic model of the operation and called it "Equilibrium Theory of Parametric Pumping". This equilibrium model consisting of linear isotherms was generalized by ARIS [3]. CAMERO and SWEED [4] expanded this theory and extended it to the domain of non-linear isotherms. This was applied by CHEN and co-workers [5, 6, 7, 8] for the description of multi-component systems, for continuous and semi-continuous processes. These models have the considerable advantage, that in their use, a computer is superfluous, the results can be calculated by simple relationships which present the concentrations of the reservoirs and the separation factors in the function of the cycle number.

Another variation in the description of operation is the so-called "Cascade Model", this was parallelly elaborated with the previously discussed one. SWEED and WILHELM [9] developed the so-called STOP-GO algorithm for the flow without component transfer, and later the component transfer without flow. The calculation of the operation was carried out by the help of a computer, successively, from cycle to cycle.

GREVILLOT and TONDEUR [10, 11] showed the analytical and graphical solution of the equilibrium cascade model of cyclic operation, the result is similar to the well known Fenske equation, used in rectification. They recognized the analogy between the rectification and parametric pumping, and they extended it for the solution of continuous operations [12].

Our previous paper [13] dealt with the separation theory of batch thermal ion exchange parametric pumping operations. The conditions of the theoretically best separation were given. In the practice this high degree of separation is hardly to attain because, the theory greatly simplifies and idealizes the real cyclic operation. Its advantage lies in the simple presentation of the component separation on an equilibrium diagram, on this, the separation mechanism of the cyclic operation is easy to understand.

In this paper the effects of some parameters of the equilibrium model on the component separation will be examined in details. For the comparison of the theoretical and the experimental results the notion of cycle efficiency is introduced, which shows very clearly the effects of operation variables on the component separation.

The Determination of Reservoir Concentration in Relation of Theoretical Cycle Number

In the batch, thermal ion exchange parametric pumping, as it was shown in previous paper [13] the best separation can be achieved if the theoretical cycles are repeated. If the "stepping up construction" is made between the equilibrium isotherms $(T_j^{i,H} \rangle T_j^{i,C})$ formed at two temperatures, between $x_{i,0}$ and $x_i=0$ interval, the concentrations of the cold reservoir, and between $x_{i,0}$ and $x_i=1$ interval, the concentration of the hot reservoir can be determined in function of the cycle number $(T_j^{i,H} \rangle T_j^{i,C})$, being equal with the number of steps. This is shown on *Figure 1.*

One step means a half cycle: the perpendicular section (x_i=constant) presents the frontal ion exchange during the flow, the inclined section gives the compositions formed during the thermostation period. The slope of the inclined section can be calculated with the help of the following balance equation, which includes the amounts of i component being in the liquid and in the resin phases, before and after the thermostation periods

$$C_0\, x_i^0\, V_k + (1-\varepsilon)\, Q\, y_i^0\, V_k = C_0\, x_i^1\, V_k + (1-\varepsilon)\, Q\, y_i^1\, V_k \qquad (1)$$

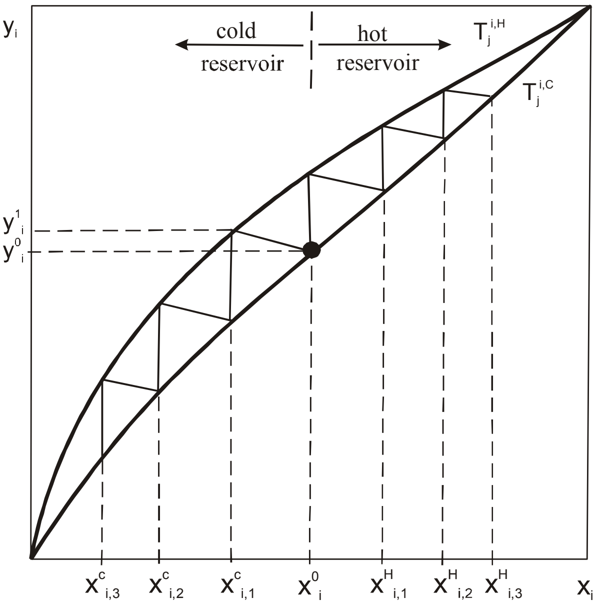

Figure 1. The change of reservoir concentrations with the theoretical cycle number

after simplification and rearrangement, the slope of the thermostation section (m) is:

$$m = \frac{y_i^0 - y_i^1}{x_i^0 - x_i^1} = -\frac{\varepsilon\, C_0}{(1-\varepsilon)\, Q} \qquad (2)$$

Starting from the composition of $x_{i,0}$ and knowing the equilibrium composition and the value of m, the „stepping up construction" can easily be made.

If graphic construction is needed, the slope of equilibrium isotherms can be optional. If the concentration domain lies over several order of magnitudes, this method is inconvenient.

In case of constant ion exchange selectivity coefficients, the equilibrium, relationship for ion exchange of two components is as follows:

$$y_i = \frac{T_j^i\, x_i}{1 + \left(T_j^i - 1\right) x_i} \qquad (3)$$

where T_j^i is constant in the function of composition and it depends definitely on the temperature. In this case the concentrations of the reservoir can directly be calculated in the function of the cycle number, but the equation is fairly complicated and can rarely be used for real systems. If the ion exchange selectivity coefficients vary with the composition, the reservoir concentration can only be determined with iterations or by the approximation of isotherms with linear sections. In our calculations the latter method was used, giving a base for a computer programme development.

The Computer Programme for the Calculation of Theoretical Cycles

In the study of parametric pumping operation, being a novel component separation possibility, one of the most important questions is, how the component separation varies during the cycles, and on the other hand when repeating cycles what the value is of the theoretically attainable separation depending only on the model parameters discussed below:

- The slope and the temperature dependence of ion exchange equilibrium isotherm, which are taken into account with the temperature dependence of ion exchange selectivity coefficients; these are the function of ion exchange resin quality and the ions to be separated, of the solution total concentration and of the applied temperature values.
- The slope "m" operating line;
- The $x_{i,0}$ initial ion composition.

To examine these parameters, a computer programme was prepared, its essence is as follows:

Using the equilibrium $T^i_j = T^i_j(y_i)$ relationships, the equilibrium isotherms are divided into small sections and are approximated with linear sections. Starting from the initial $x_{i,0}$ composition, in both direction, between the isotherms, the „stepping up construction" is made until the previously given cycle number is reached. The new x_i composition is given by the intersection of the straight line (thermostation) of "m" slope and the appropriate linear section of the isotherm.

The equilibrium relations can be optional, in the calculations of real systems, third order polynoms are used, fitted previously on experimentally determined data points, with the required accuracy [21].

In these calculations, as constants were taken the free volume coefficient of fixed bed ion exchange resin column (ε=0.35) and the resin capacity (Q=2.36 mequ/cm^3), these data were determined with Ca^{2+} loaded VARION KSM ion exchange resin particles, settled in water.

In these calculations, the isotherms were approximated with linear sections, the y_i co-ordinate was splitted to sections, these sections were shortened until the concentration difference of the reservoirs went below 1%. Depending on the shape of the isotherms, the number of the sections reached 50 to 100.

Outputs of the program are: the compositions of the cold and hot reservoirs in the function of theoretical cycle number, and the separation factors.

The Result of Calculations

Parameter Sensitivity Investigation

Selecting constant ion exchange selectivity coefficients in the function of resin composition, the effects of the following parameters were investigated:

- The ratio of selectivity coefficients, formed on ion exchange on two temperature values (*Figure 2.*);

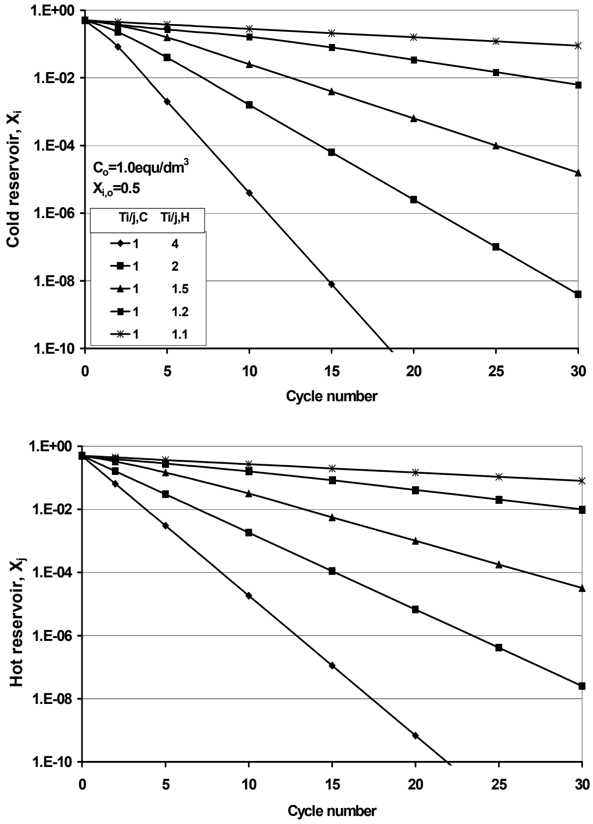

Figure 2. The effect of the ratio of selectivity coefficients on the change of reservoir concentration

- The absolute value of selectivity coefficients (*Figure 3.*);

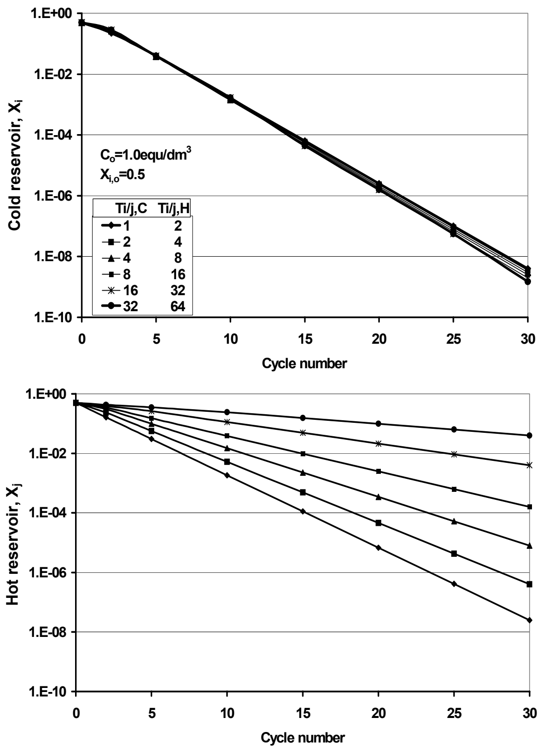

Figure 3. The effect of absolute values of selectivity coefficients on the reservoir concentration

- The total concentrations of solutions (*Figure 4.*);

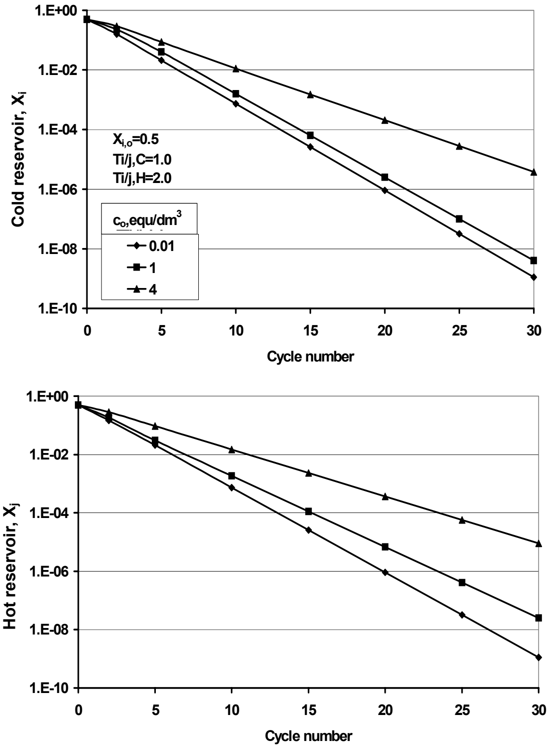

Figure 4. The effect of solution total concentration on the reservoir concentration

- Initial ion composition (*Figure 5.*).

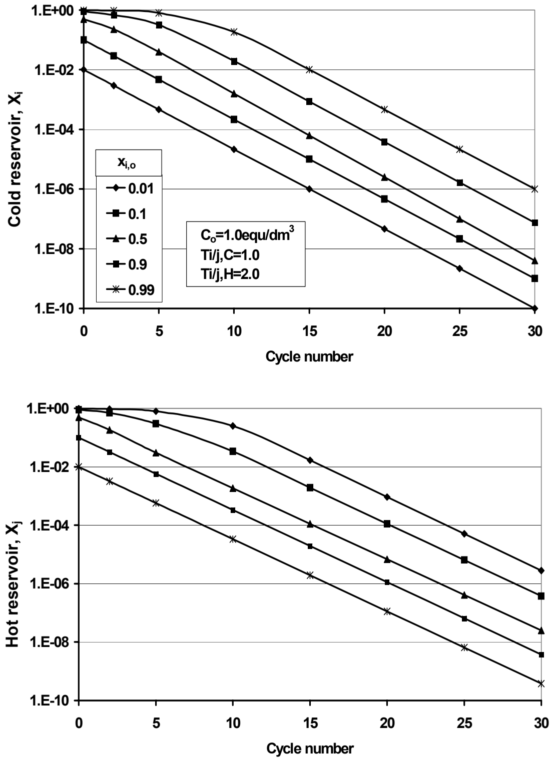

Figure 5. The effect of initial ion concentration on the change reservoir concentration

On the figures the logarithmic values of ion composition of reservoirs are shown in the function of cycle number. It can be seen that if x_i, x_j<0.1, then the compositions exponentially decrease with the cycle number.

From the results, the following deductions can be made being valid for thermal parametric pumping operations;

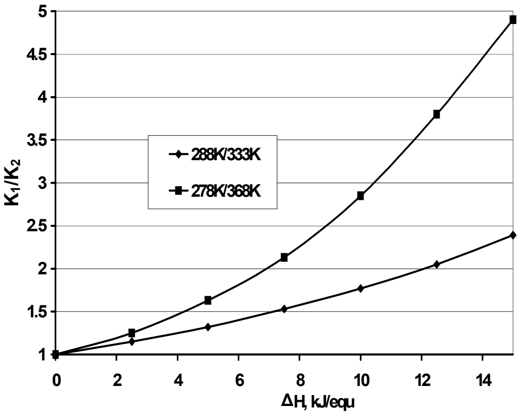

Figure 6. The ratio of ion exchange equilibrium constants in the function of the enthalpy change of ion exchange reactions

1. The value of selectivity coefficients ratio determines basically the variation of reservoir composition in function of the cycle number. (*Figure 2.*)

   The temperature dependence of the selectivity constants is basically related to the energy changes following the ion exchange processes. The temperature dependence of the equilibrium constant of ion exchange reaction can be described by van't Hoff's equation, its integral form is:

   $$\ln K = \frac{\Delta H}{RT} + C \tag{4}$$

   It is evident that the enthalpy change of the ion exchange reaction, is an essential postulation of the realization of parametric pumping operation. On *Figure 6.,* using Equation (4), the ratio of equilibrium constants is plotted against the ion exchange reaction enthalpy change. In case of exchange of ions having the same valence number, the ratio of equilibrium constants is approximately the same as the ratio of selectivity coefficients.

   The enthalpy changes of some ion exchange reactions are listed in *Table 1.* [14, 15, 16, 17, 18, 19, 20]. It shows that in most cases, especially if 90K temperature difference is applied, the separation of ion pairs with thermal parametric pumping seems to be very attractive.

2. The absolute values of selectivity coefficients have considerable influence on the decrease of ion ratio of unfavourably bonding components, but they are ineffective for the same one of the well bonding components (*Figure 3.*). These phenomena can be explained by the slope "m" of operating line, being constant with the composition and, with the slope of isotherms, depending strongly on the composition and the absolute value of selectivity coefficients.

   The logarithmic values of reservoir compositions, shown on *Figures 2.* to *5.* in the case of x_i, x_j<0.1, are inversely proportional to the cycle number, if half-logarithmic log x scale is selected. In the concentration intervals of $0 < x_i < 0.1$ and $0.9 < x_i < 1$, the ion exchange isotherms are nearly linear. This shows that the computation can greatly be simplified (*Figure 7.*).

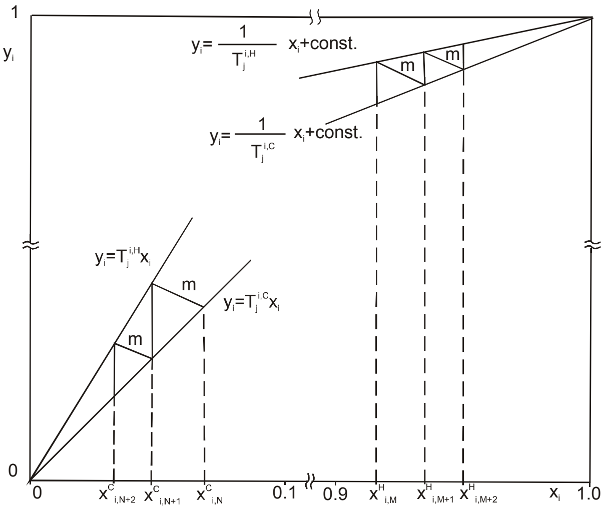

Figure 7. The linearization of ion exchange isotherms and the reservoir concentrations in the case of x_j, x_i <0.1

Table 1. The enthalpy changes of some ion exchange reactions

Ion pair	Ion exchanger resin	ΔH KJ/equ	Ion pair	Ion exchanger resin	ΔH KJ/equ
Na^+-H^+	Dowex 50×12	4,64	Y^{3+}-Ce^{3+}	Dowex 50×8	-2,33
K^+-H^+	- “ -	8,96	La^{3+}-Na^+	Dowex 50×4	7,37
Rb^+-H^+	- “ -	11,68	La^{3+}-Ce^{3+}	Dowex 50×8	-0,19
Cs^+-H^+	- “ -	14,23	Ce^{3+}-K^+	- “ -	-8,10
Be^{2+}-H^+	- “ -	-2,59	Ce^{3+}-Be^{2+}	- “ -	2,60
Be^{2+}-H^+	- “ -	4,56	Ce^{3+}-Cr^{3+}	Dowex 50×2	0,77
Co^{2+}-H^+	- “ -	-0,42	- “ -	Dowex 50×8	1,15
Zn^{2+}-H^+	- “ -	-0,42	- “ -	Dowex 50×16	1,36
Cu^{2+}-H^+	- “ -	2,52	Pr^{3+}-Ce^{3+}	Dowex 50×8	0,16
La^{3+}-H^+	- “ -	2,39	Nd^{3+}-Ce^{3+}	- “ -	0,092
Eu^{3+}-H^+	- “ -	3,60	Sm^{3+}-Ce^{3+}	Dowex 50×4	1,22
Pm^{3+}-H^+	- “ -	1,23	Eu^{3+}-Ce^{3+}	Dowex 50×8	-1,82
Tm^{3+}-H^+	- “ -	1,97	Gd^{3+}-Ce^{3+}	- “ -	-2,36
Lu^{3+}-H^+	- “ -	1,73	Tb^{3+}-Ce^{3+}	- “ -	-2,89
K^+-Na^+	- “ -	3,78	Dy^{3+}-Ce^{3+}	- “ -	-2,75
Rb^+-Na^+	- “ -	2,42	Ho^{3+}-Ce^{3+}	- “ -	-2,49
Cs^+-Na^+	- “ -	3,24	Er^{3+}-Ce^{3+}	- “ -	-1,98
Ba^{2+}-Na^+	- “ -	3,51	Tm^{3+}-Ce^{3+}	- “ -	-1,43
	Izotópok	j/eq	Yb^{3+}-Ce^{3+}	- “ -	-1,08
$^{6}Li^+$-$^{7}Li^+$	Dowex 50×12	-9,46	Lu^{3+}-Ce^{3+}		-0,64
$^{22}Na^+$-$^{24}Na^+$	- “ -	-1,72	Cl^-- SO_4^{2-}	Amberlite IRA-400	15,0
$^{40}Ca^{2+}$-$^{48}Ca^{2+}$	- “ -	-2,9			
$^{35}Cl^-$–$^{37}Cl^-$	BioRad AG1-X10	-6,1 (0-10°C)			
- “ -	- “ -	-0,61 (20-60°C)			

Instead of the relationship, generally describing the equilibrium of ion exchange reaction
in the interval of

$$0 < x_i < 0.1, \text{ the}$$

$$y_i = T_j^i \, x_i \tag{5}$$

and in the interval of

$$0.9 < x_i < 1, \text{ the}$$

$$y_i = \frac{1}{T_j^i} x_i + C \tag{6}$$

relationships can be used, these were derived from Eq.(3), taking the limits of $x \rightarrow 0$ and $x \rightarrow 1$. With its help it is easy to show that the following simple relationships can be used for the description of the alteration of reservoir concentrations; in the case of $T_j^{i,H} > T_i^{i,C} > 1$, for the subsequent cycles:
The concentration of "i" ions in the cold reservoir is:

$$x_{i,n+1}^{C} = x_{i,n}^{C} \frac{T_j^{i,C} - m}{T_j^{i,H} - m} \tag{7}$$

The ion ratio of "j" in the hot reservoir is:

$$x_{j,n+1}^{H} = x_{j,n}^{H} \frac{\dfrac{1}{T_j^{i,H}} - m}{\dfrac{1}{T_j^{i,C}} - m} \tag{8}$$

Equation (7) describes the alteration of ion ratio of "i" ions bonding advantageously, during the theoretical cycle, in the cold reservoir. It can be seen that the increase of the absolute values of selectivity coefficients increases the attainable separation within a theoretical cycle. It is noted that the usual values of T_j^i are between 2 and 50; the value of "m" lies between (-0.01) and (-0.2); in these cases the theoretically attainable separation increases only slightly with the growing values of selectivity coefficient.
Equation (8) describes the alteration of ion ratio of unfavourable bonding "j" ions within a theoretical cycle, in the hot reservoir. It can be seen that reciprocal values of the selectivity coefficients are present in the fraction, these values can be compared to values of "m", and the increase of selectivity coefficients considerably decreases the separation attained within a step.

3. From Equations (7) and (8), it can be seen that the growing value of "m" decreases the separation in both reservoirs attained within a step (*Figure 4).* The value of "m" is given by Equation (2).
   While decreasing the absolute value of "m" the separation is better, therefore it is advantageous to use for the separation high capacity ion exchange resin. The free volume coefficient (ε) of ion exchange columns is usually between 0.3 and 0.4. Decreasing the total concentration of the solution, the attainable separation within a step is better, but the amount of ions processed in unit time, generally decreases.

4. Investigating the effect of initial ion composition from the viewpoint of theoretical cycles it can be concluded that fewer cycles are needed to reach the same separation at smaller initial compositions. (*Figure 5.*).

Summarizing, for the calculation of component separation, based on theoretical cycles, the following simple relationship can be used. This presents the concentration of the reservoirs in the case of x_i, $x_j < 0.1$ ion ratios, with less than ±5% error. In case of cold reservoir, for advantageously bonding "i" ions:

$$x_{i,N}^{C} = x_{i,0} \left[\frac{T_j^{i,C} - m}{T_j^{i,H} - m} \right]^N \qquad \left(T_j^{i,H} > T_j^{i,C} > 1 \right) \tag{9}$$

In the case of hot reservoir, for weakly bonding "j" ions:

$$x_{j,N}^{H} = x_{j,0} \left[\frac{\dfrac{1}{T_j^{i,H}} - m}{\dfrac{1}{T_j^{i,C}} - m} \right]^N \qquad \left(T_j^{i,H} > T_j^{i,C} > 1 \right) \tag{10}$$

It is noted, if the selectivity coefficients $\left(T_j^{i,C}, T_j^{i,H} \right)$ are dependent on the ion composition of the resin and/or the liquid phases, then in the intervals of $0 < x_i < 0.1$ and $0 < x_j < 0.1$ (Equ. 10), the mean values of $T_j^{i,C}$ and $T_j^{i,H}$ should be used.

Summary

In this paper the component separation theory is presented, which describes the batch, thermal ion exchange parametric pumping process. In the frame of this, simple relationships are presented; these describe the alteration of reservoir concentrations in the function of the theoretical cycle number.

Calculations were made to investigate the effects of the ratio and absolute value of ion exchange selectivity coefficients, the total concentration of solution and the initial ion composition on the component separation.

The simplified model gives only rough estimation of the transient concentration changes and elucidates the effects of some process and operation parameters playing an important role in the production of high purity compounds. One major benefit of the equilibrium model is that it provides view in the mechanism of the separation.

SYMBOLS

m	variable, defined by Equ. (2)
x_j	ion ratio of component "j" in the liquid phase
$x_{j,0}$	initial ion ratio of component "j" in the liquid phase
$x^H_{i,N}$ $x^C_{i,N}$	ion ratio in hot and cold reservoirs, in the N^th theoretical cycle
y_j	ion ratio of component "j" in resin phase
C_0	total concentration of liquid phase
ΔH	enthalpy change of ion exchange process
K_1, K_2	equilibrium constants of ion exchange reaction on two, different temperatures
L	the length of ion exchange column
N	theoretical cycle number
Q	capacity of ion exchanger resin, related to volume unit
$T_j^{i,C}$ $T_j^{i,H}$	ion exchange selectivity coefficient of ion "i", related to ion "j", on "cold" and "hot" temperatures
V_k	volume of ion exchanger resin charged into the column
ε	free volume coefficient of the ion exchanger resin column

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