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SEPARATION BY ION EXCHANGE AND ADSORPTION PARAMETRIC PUMPING V.

Cycle Efficiency for Batch, Thermal Ion Exchange Parametric Pumping

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The theoretically best attainable separation can easily be determined in the function of the theoretical cycle number. In the reality, due to the non-equilibrium ion exchange, the mixing phenomena and the "run out" of characteristics, the performance of the actual process, especially in the production of high purity materials, a cycle efficiency value can be ordered to the parametric pumping processes. The authors investigated the relationships between the more important process and operation parameters and the cycle efficiency in aqueous media and in the presence of VARION-KSM ion exchange resin, Ca^{2+}, K^+ cations and Cl^- anions.

Introduction

Production of high purity materials accounts for the major production cost in fine chemical industries. There has been a growing demand for economical and energy-efficient separation processes. The increasing interest in this area is also reflected in the numerous research articles published in the field of ion exchange and adsorption separations [1-5]. Among these processes parametric pumping is a technique which has been studied extensively [6-8]. The most important property of this process is the fact that it is a reagent-free separation process in which no regeneration chemicals are needed which may pollute the environment, and in which no regenerant can contaminate either product.

Emphasis is placed on the following areas:

- Development of adsorbents and ion exchange materials [3-4, 9-10].
- Investigation of possible thermodynamic parameters [11-13].
- An improved theoretical understanding of the process [14-15].
- Development of new process configurations [16-17].
- Development of highly efficient processes [18].

In this paper experimental data were compared with the best attainable separation achieved by the application of theoretical cycles. Cycle efficiency (η_i) was defined as the ratio of the theoretical and actual cycle numbers. It presents an interesting possibility in the evaluation of experimental results, especially in the production of high purity ionic compounds.

Experimental part

An aqueous solution of calcium and potassium cations in the presence of chloride anion on a highly acidic cation exchanger (Varion-KSM, Nitrochemical Works of Balatonfűzfő, Hungary) was selected as a model system.

The ion exchange isotherms were determined by simple batch equilibration of a known mass of resin with a given volume of solution of known concentration and ionic composition over 36 hours at temperatures 288K and 333K. The solution was then separated from the resin and the concentration of calcium and potassium in solution were measured. The ion exchanger phase concentration was calculated by mass balance. A preliminary summary of these data have been reported elsewhere [19]. The experimentally determined ion exchange isotherms and the ion exchange selectivity coefficient (T_K^{Ca}) as a function of resin phase composition (y_{Ca}) are shown in Figs. 1-3.

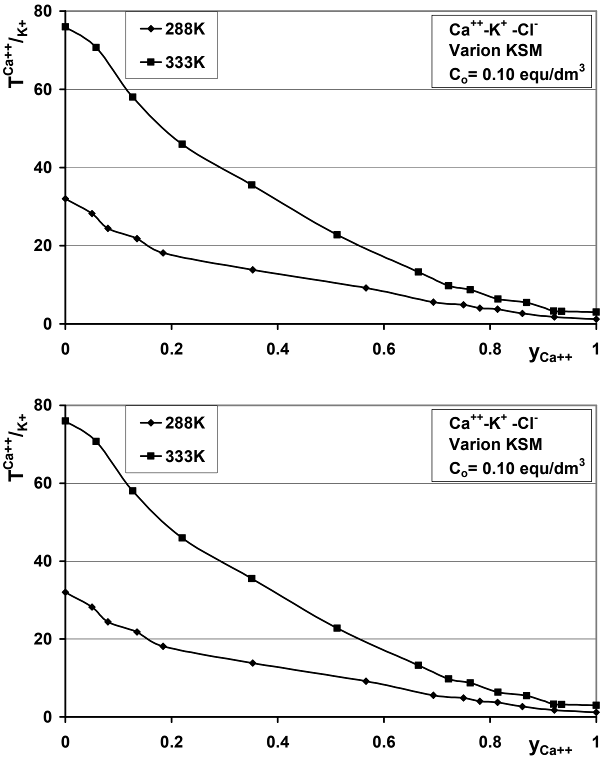

Figure 1. Ion exchange equilibrium of Ca^{2+} -K^{+} cations at temperatures of 288K and 333K, with a total cation content of 0.10 equ/dm^3

Knowledge of ion exchange isotherms at two temperatures is required numerically for the mathematical modelling of the process. In our case, the ion exchange selectivity coefficient (T_K^{Ca}) as a function of resin phase composition (y_{Ca}) was used for the definition of ion exchange equilibrium. The equilibrium data were fitted to a third degree polynome of the following form:

$$T_K^{Ca} = a\,y_{Ca}^3 + b\,y_{Ca}^2 + c\,y_{Ca} + d \qquad (1)$$

A least square optimization of the equilibrium data gave the constants of Eq.(1). These functions and constants were used in all calculations (Table 1.).

Table 1. Constants of the ion exchange selectivity coefficient at two temperatures

	C_0=0.10equ/dm^3		C_0=0.50equ/dm^3		C_0=1.0equ/dm^3	
	288K	333K	288K	333K	288K	333K
a	-38.17	26.55	-0.727	-14.9	5.485	5.99
b	99.12	7.25	12	33.28	-8.063	-8.748
c	-100.4	-100.2	-22.89	-38.9	0.596	-0.936
d	40.65	70.03	12.15	21.2	2.186	4.02

The parametric pumping experiments were carried out in a laboratory scale, automatic apparatus, described in detail in the previous paper [20]. Different size glass columns with jacket and reservoirs are included in the system for direct heat transfer experiments.

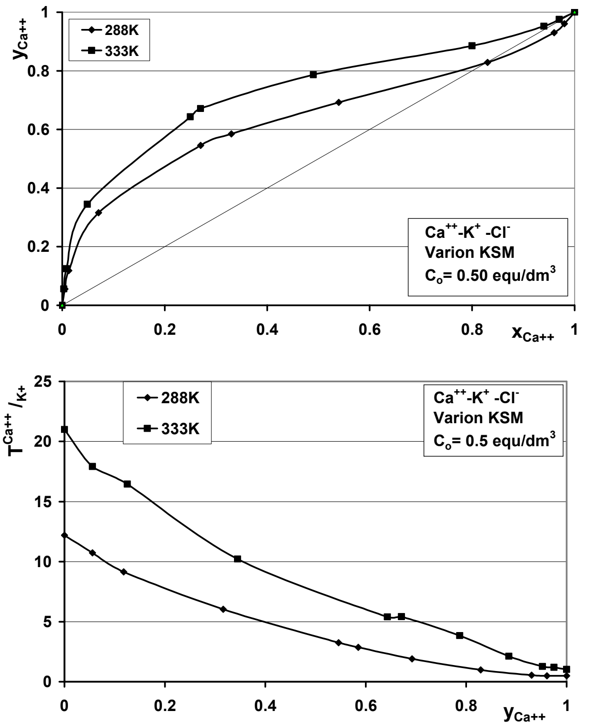

Figure 2. Ion exchange equilibrium of Ca^{2+} -K^{+} cations at temperatures of 288K and 333K, with a total cation content of 0.50 equ/dm^3

The effect of the following more important operation and process parameters were investigated:

- Liquid flow rate (v_o, from 0. 1 to 2. 3 m/s)
- Transfer of ion fraction during a half cycle(α', from 0.026 to 1.0 (dimensionless))
- Initial ion composition ($x_{Ca,0}$, from 0.2 to 0.8)
- Length of ion exchanger column (L, from 0.5 to 1.5m)
- Total solution concentration (C_0, from 0.1 to 1.0 equ/dm^3).

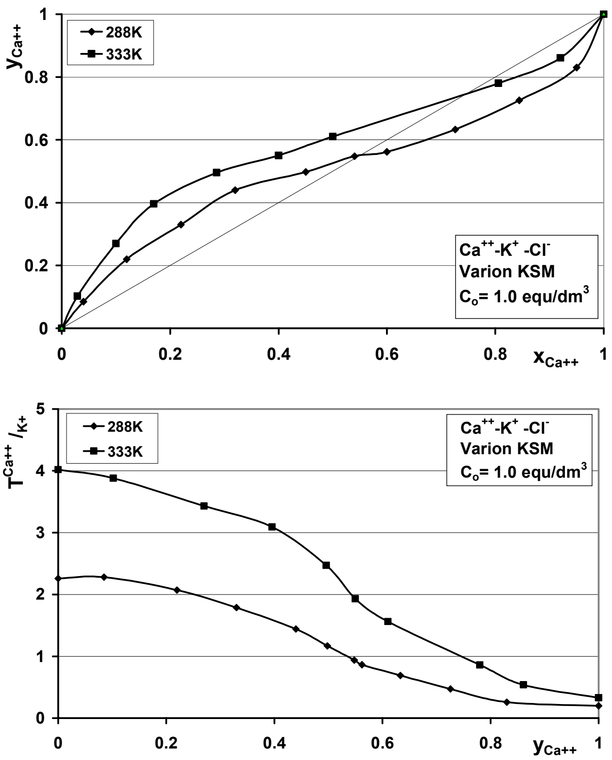

Figure 3. Ion exchange equilibrium of Ca^{2+} -K^+ cations at temperatures of 288K and 333K, with a total cation content of 1.0 equ/dm^3

The following variables and operational conditions were fixed:

- The temperatures (288K and 333K) in cold and hot half cycles
- Particle size of ion exchanger, d_p = 0,5-0,7 mm
- Initial condition of the experiments, the ion exchanger column was always brought into equilibrium at the lower temperature (288K) with the solution to be separated
- Location of the cold reservoir and the hot reservoir, in our case, the hot reservoir was always connected to the upper part of the column
- Length of thermostating time is 15 minutes in case of a column diameter of 28 mm and, 8 minutes in case of a 10 mm column diameter
- Dead-volume of the equipment.

According to the temperature dependence of the ion exchange equilibrium, the concentration of calcium ions decreased in the cooled reservoir (288K). In the other case the concentration of potassium ions decreased in the heated reservoir (333K). The total cationic concentration of the solution in the mentioned reservoirs was constant.

A part of the experimental results and data was published in the previous paper [20]. Table 2-4 summarizes the investigated parameters and results for selected experiments at three solution concentrations. Publication of about 1000 determined reservoir concentration from 45 measuring series is not possible here, only the hot and cold reservoir concentrations of the 20th cycle are given.

The Comparison of the Calculated and Experimental Results

Using relationships presented previously for a given parametric pumping operation, the theoretically best attainable separation can easily be determined in the function of the cycle number. Knowing this, it presents an interesting possibility in the evaluation of experimental results as it is shown below.

Among the experimental data, the reservoir concentrations of the 20th cycle were taken as basic data. (The sensitivity of the used ZEISS-AAS1 atomic absorption spectrophotometer was

Table 2. Conditions and results for selected batch experiments at 0.10equ/dm^3 solution concentration, L=1.0m, D_b=28mm

No.	$X_{ca,0}$	ΔV,dm^3	B,dm^3/h	C_{20} ,mequ/dm^3	N_T	η_i	P_{20} ,m/m%
		α'	v_o,mm/s	Ca^{2+}	Ca^{2+}	Ca^{2+}	K^+
				K^+	K^+	K^+	Ca^{2+}
1	0.20	0.4	1.0	0.038	9.8	0.49	99.981
		0.026	0.45	6.07	6.6	0.33	88.555
2	0.20	0.8	1.0	0.034	10.4	0.52	99.983
		0.052	0.46	2.05	8.6	0.43	95.982
3	0.20	2	1.0	0.026	11.6	0.58	99.987
		0.13	0.45	1.12	9.8	0.49	97.785
4	0.20	4	1.0	0.022	12.2	0.61	99.989
		0.26	0.43	7.76	6.2	0.31	85.598
5	0.20	6	1	0.019	12.6	0.63	99.990
		0.39	0.45	22.7	4.4	0.22	62.999
6	0.20	8	1	0.018	12.8	0.64	99.991
		0.52	0.44	45.1	2.6	0.15	37.836
7	0.50	0.4	1.0	0.1	10.4	0.5	99.971
		0.026	0.44	0.025	13.6	0.68	99.950
8	0.50	0.8	1	0.052	10.6	0.53	99.974
		0.052	0.45	0.02	13.8	0.69	99.960
9	0.50	2	1	0.045	11.1	0.55	99.977
		0.13	0.45	0.015	14.4	0.72	99.970
10	0.50	4	1	0.033	11.4	0.57	99.983
		0.26	0.47	1.28	7.2	0.36	97.472
11	0.50	6	1	0.88	6.4	0.32	99.558
		0.39	0.45	5.95	5	0.25	88.768
12	0.50	8	1	8.55	3.6	0.18	95.534
		0.52	0.45	13.8	3	0.15	75.747
13	0.80	0.8	1	0.68	9	0.45	99.659
		0.052	0.46	0.0033	14.4	0.72	99.993
14	0.80	2	1	13.4	5.4	0.27	92.819
		0.13	0.45	0.0025	15.4	0.77	99.995
15	0.80	4	1	38	3.2	0.16	76.543
		0.26	0.45	0.002	15.8	0.79	99.996
16	0.80	6	1	50.2	2.4	0.12	66.489
		0.39	0.44	0.27	7.2	0.36	99.461
17	0.80	8	1	58	1.8	0.09	59.155
		0.52	0.45	1.86	3.8	0.19	96.348

inadequate for the accurate determination of the low concentration of given component, after the 20th cycle). Using the calculated data, the theoretical cycle number of the former reservoir concentrations was determined, and the cycle efficiency (η_i) was defined as the ratio of the theoretical and actual cycle numbers. It is shown in the function of process parameters for Ca^{2+}–K^+ ion pairs, in the presence of Cl^- anions, and in the case of VARION KSM cation exchanger resin.

Table 3. Conditions and results for selected batch experiments at 0.50equ/dm^3 solution concentration, L=1.53m, D_b=28mm, ΔV=800cm^3, α'=0.17

No.	$X_{Ca,0}$	B,dm^3/h v_o,mm/s	C_{20} ,mequ/dm^3 Ca^{2+} K^+	N_T Ca^{2+} K^+	h_i Ca^{2+} K^+	P_{20} ,m/m% K^+ Ca^{2+}
1	0.20	0.2 0.09	0.014 0.92	15.6 9.2	0.78 0.46	99.999 99.908
2	0.20	0.4 0.18	0.018 0.88	15 9.4	0.75 0.47	99.998 99.912
3	0.20	0.7 0.32	0.02 14.9	14.8 5.6	0.74 0.28	99.998 98.487
4	0.20	1.1 0.51	0.025 20.7	14.4 4.2	0.72 0.21	99.997 97.886
5	0.20	1.6 0.71	0.032 23.2	13.2 3.6	0.66 0.18	99.997 97.625
6	0.20	2.8 1.24	0.74 25.1	7.6 3.2	0.38 0.16	99.926 97.425
7	0.50	0.4 0.18	0.11 0.07	13.6 12.2	0.68 0.61	99.989 99.993
8	0.50	0.7 0.31	0.24 0.11	12.2 11.2	0.61 0.56	99.976 99.989
9	0.50	1.1 0.50	0.56 0.83	8.6 8.2	0.43 0.41	99.944 99.917
10	0.50	1.6 0.71	0.76 2.1	6.4 7.6	0.32 0.38	99.924 99.790
11	0.50	2.8 1.24	0.9 6.8	4.8 4.8	0.24 0.24	99.910 99.315
12	0.80	0.4 0.18	4.2 0.004	9.6 16.6	0.48 0.83	99.578 99.999
13	0.80	0.7 0.31	14.9 0.005	8 16.2	0.4 0.81	98.487 99.999
14	0.80	1.1 0.48	38.7 0.01	5.4 15.5	0.27 0.77	95.974 99.999
15	0.80	1.6 0.71	44.2 0.025	4.8 13	0.24 0.65	95.376 99.997
16	0.8	2.8 1.22	51.5 0.23	4.2 8.2	0.21 0.41	94.570 99.977

In *Figure 4* is shown the effect of flow rate, in case of 0.5 equ/dm^3 solution concentrations, if various initial ion compositions are used. The cycle efficiency was increasing with the decrease of flow rate but, the measure of growth and the values of cycle efficiencies varied widely.

If the initial ion composition is low, then cycle efficiency generally increases for a given ion and the effect of flow rate is small.

In *Figure 5* are shown the values of cycle efficiency as a function of the relative ion amount (α') correspond to a half cycle, in case if various initial ion compositions and 0.1 equ/dm^3 solution concentration. The curves reach maxima, indicating the lack of equilibrium. The place of the maxima shows the amount of relative ions (α'), which should be the load for the best separation. The role of the initial ion composition is clear: The maximum place of the given component is shifted to the larger loads, proportionally to the decrease of the initial ion composition.

Table 4. Conditions and results for selected batch experiments at 1.0equ/dm^3 solution concentration, L=1.50m, D_b=10mm, B=0.087dm^3/h, v_0=0.31mm/s

No.	$X_{ca,0}$	ΔV,dm3 α'	C_{20} ,mequ/dm3 Ca^{2+} K^+	N_T Ca^{2+} K^+	η_i Ca^{2+} K^+	P_{20} ,m/m% K^+ Ca^{2+}
1	0.20	0.1 0.17	0.035 6.01	16.1 10.6	0.80 0.53	99.998 99.699
2	0.20	0.1 0.34	0.01 10	18 9.6	0.9 0.48	99.999 99.497
3	0.20	0.2 0.68	0.01 426	18 3.4	0.9 0.17	99.999 72.935
4	0.20	0.3 1	0.01 552	18 2.4	0.9 0.12	99.999 61.878
5	0.50	0.1 0.17	0.65 3.96	13.8 9.4	0.7 0.47	99.967 99.802
6	0.50	0.1 0.34	0.13 0.17	16.4 15.6	0.82 0.78	99.993 99.991
7	0.50	0.2 0.68	0.18 0.08	15.8 16	0.79 0.8	99.991 99.996
8	0.50	0.3 1	76.80 131.00	5 3.2	0.25 0.16	96.007 92.991
9	0.80	0.1 0.17	2.72 0.65	13.2 11.6	0.66 0.58	99.864 99.967
10	0.80	0.1 0.34	1.12 0.01	15 17.2	0.75 0.86	99.944 99.999
11	0.80	0.2 0.68	354 0.006	3.6 18.2	0.18 0.91	78.493 99.999
12	0.80	0.3 1	500.3 0.61	2.4 11.8	0.12 0.59	66.640 99.969

In *Figure 6* are shown the effects of the above discussed components in case of 1 equ/dm^3 solution concentration. The results are the same as above, besides the considerably greater loads.

In *Figure 7* the effects of the total concentration of solutions are presented in the function of relative ion amounts, flown through during a half cycle. With the increase of solutions total concentration, markedly increases the cycle efficiency belonging to the maxima of the curves on one hand, while on the other hand the maximum cycle efficiencies appear always at higher loads of relative ion amounts.

The equilibria related to Ca^{2+}–K^+ ion pairs depends strongly on the total concentration of solutions (Fig. 1-3.). Increasing the concentration, the selectivity values decrease and the isotherms of the so called sigmoid shape form. *Figure 7* proves that the decrease of selectivity values improves the load of the column.

Due to the sigmoid type isotherm, at the concentration of 1 equ/dm^3, the shape and the

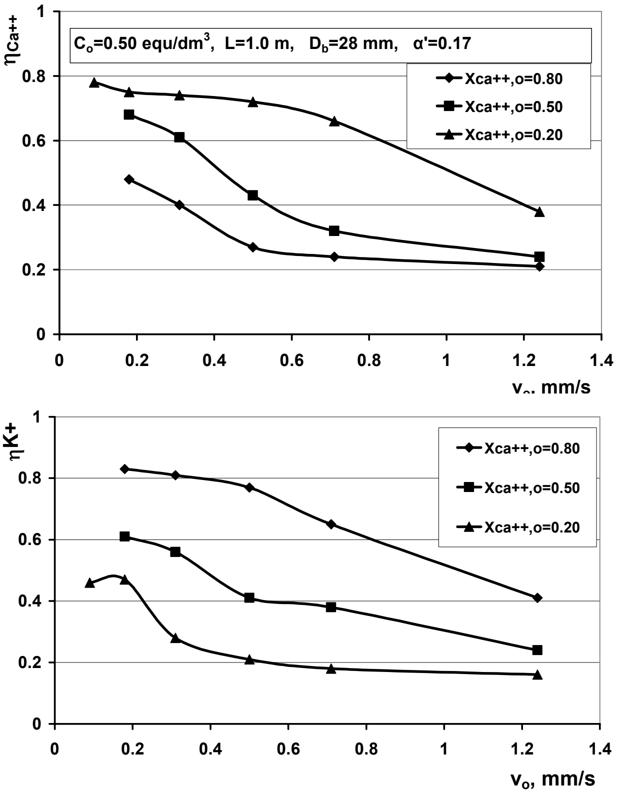

Figure 4. The changes of cycle efficiencies in the function of the flow rate

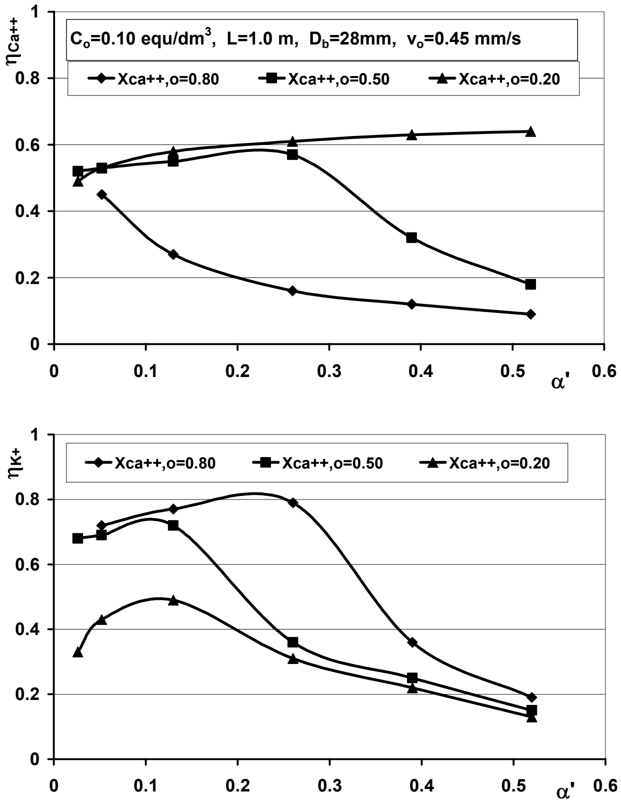

Figure 5. The changes of cycle efficiencies with α’ at different initial ion composition and at 0.1 equ/dm^3 solution concentration

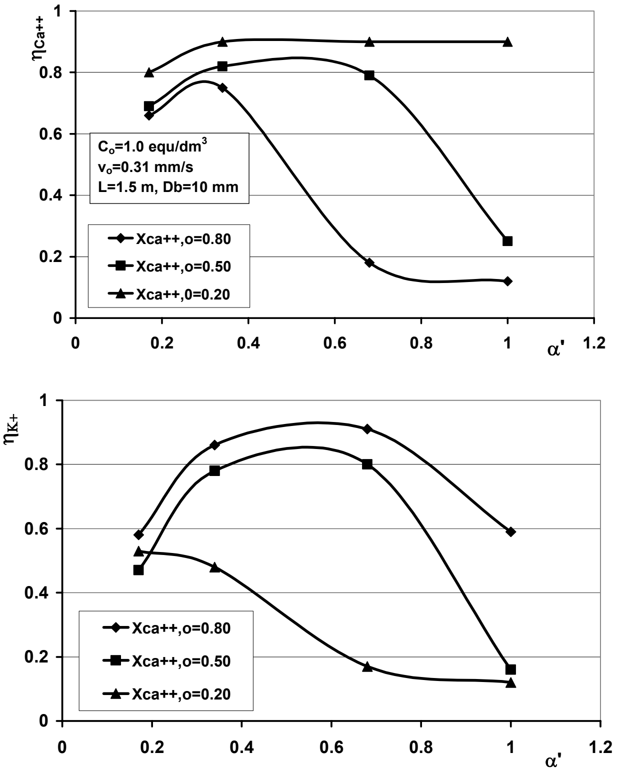

Figure 6. The changes of cycle efficiencies with α’ at different initial ion composition at 1 equ/dm^3 solution concentration

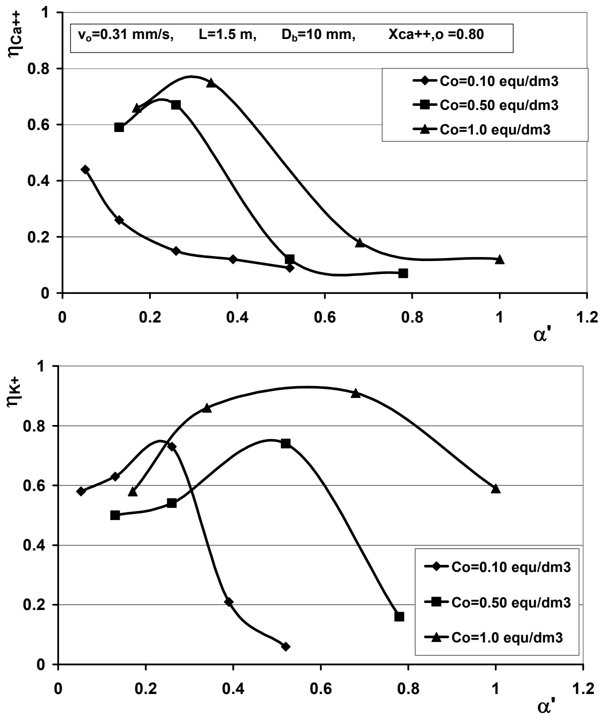

Figure 7. The changes of cycle efficiencies with different solution concentration

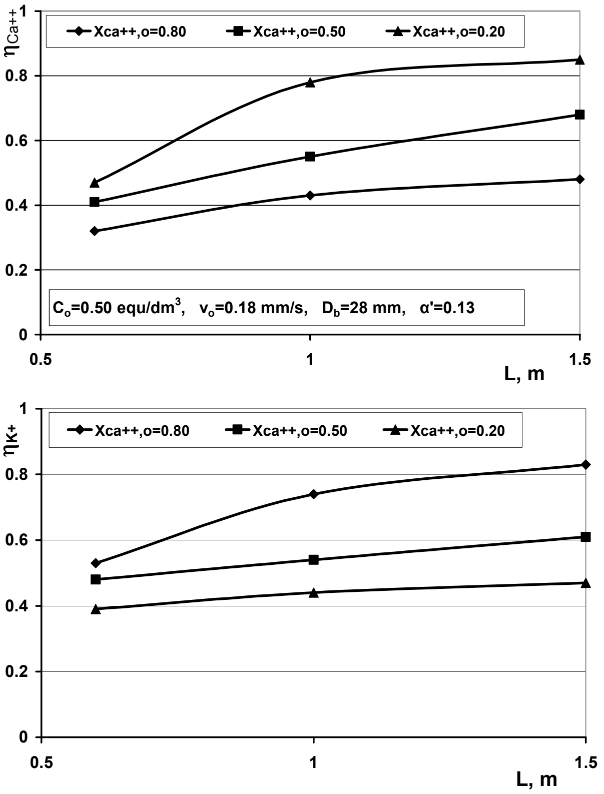

Figure 8. The changes of cycle efficiency with the length of ion exchange column

position of cycle efficiency curves of Ca^{2+} and K^+ are very similar, this is very advantageous, because the column can be operated with optimum load regarding both the ions.

At last, in *Figure 8* are shown the change of cycle efficiencies as a function of column height, in case of 0.5 equ/dm^3 initial concentration and different initial ion composition. The cycle efficiencies increase in different extent with the column height. In given circumstances, the number of equilibrium units formed in the column is proportional with the length of the ion exchanger charge, filled in the column. This basically determines the level of the component separation.

Summary

The results of these calculations were used in the evaluation of results determined in the experiments with Ca^{2+}–K^+ ion pair, the idea of cycle efficiency was defined. This is the ratio of the theoretical and practical cycle numbers belonging to a given reservoir concentration. With the help of the cycle efficiency, diagrams were constructed to elucidate the effect of some operation parameters on the component separation.

With the selection of appropriate parameters and starting concentration in favourable composition range, the cycle efficiencies remain high, and the products purity reach the 99.99 or 99.999 m/m% values.

SYMBOLS

v_0	superficial velocity of liquid phase
x_j	ion ratio of component "j" in the liquid phase
$x_{j,0}$	initial ion ratio of component "j" in the liquid phase
y_j	ion ratio of component "j" in resin phase
C_0	total cationic concentration of liquid phase
$C_{20,j}$	reservoir concentration of component "j" after the 20th cycle
L	the length of ion exchange column
N_T	theoretical cycle number
$P_{20,j}$	product purity of component "j" after the 20th cycle
T_j^i	ion exchange selectivity coefficient of ion "i", related to ion "j"
ΔV	volume flow through in half cycle
α'	dimensionless ion proportion, the ratio of cation amount flowing through during half cycle and ion exchange capacity of the column
η_i	cycle efficiency related to component "i"

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