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J. E. Sabadell[a]; N. H. Sweed[a]
[a] CHEMICAL ENGINEERING DEPARTMENT, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY

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Parametric Pumping with pH

J. E. SABADELL and N. H. SWEED
CHEMICAL ENGINEERING DEPARTMENT
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY 08540

Summary

Separations of aqueous solutions of Na^+ and K^+ have been obtained using a recuperative pH parametric pumping system. A chromatographic column of cation exchange resin was subjected simultaneously to an alternating axial displacement of solution and to an alternating pH gradient. The synchronous coupling of these two actions produced a concentration enrichment of 15–80% above the feed.

INTRODUCTION

The parametric pumping separations which have been reported recently (*1–4*) all have used an alternating temperature field for their energy source. The parametric pumping principle, however, does not restrict the form the energy must take. Any intensive variable that affects the equilibrium distribution of the component being separated is acceptable. It is expected, therefore, that electrical, magnetic, and chemical energy can be used instead of temperature to drive the separation process.

In the present communication it is demonstrated how *chemical energy* may be harnessed to effect parametric pumping separations. Specifically, an alternating pH gradient has been imposed on a column of cation exchange particles to separate solutions of Na^+ and of K^+.

BACKGROUND

The principle of parametric pumping separation requires that two synchronous, periodic, alternating mass fluxes be coupled in such a way that they act at right angles to one another. Why and how this coupling produces a separation has been discussed previously (*2*), along with a broad review of the subject. For the purpose of this report, however, it is sufficient that the reader understand the four basic requirements for implementing the parametric pumping principle (i.e., forming a process from it):

1. The existence of a two-phase system.
2. An equilibrium distribution of the component being separated between the phases.
3. An alternating relative velocity between the phases.
4. An alternating interphase mass flux obtained by periodically changing one or more of the intensive thermodynamic variables that affect equilibrium.

The number of parametric pumping processes that can be developed within the framework of these requirements is very large. To date, however, most investigations have been limited to solid–liquid systems (Requirement 1) with adsorption or ion exchange equilibrium distributions (Requirement 2). The alternating relative velocities (Requirement 3) have been produced by pumping liquid solution back and forth over the solid phase, which is held fixed in a chromatographic column. The fourth requirement has always been satisfied by using an oscillating temperature field because this has a marked effect on equilibrium distributions.

In the present work, however, we replace the thermal field with an alternating pH field; thus we satisfy the fourth requirement by using chemical energy. This system can be applied to situations where thermal degradation is a problem, for example. We emphasize that the Na^+ and K^+ separations presented here are only *examples* of the technique. No attempt at optimization has been made thus far.

Because many of the concepts in pH parapumping were developed from the thermal system, let us first review thermal parametric pumping.

THERMAL PARAMETRIC PUMPING

Two quite different methods of imposing temperature fluctuations have been studied: the "recuperative" thermal mode and the "direct" thermal mode.

The recuperative thermal mode was first discussed in 1966 (*1*). In this mode each end of a column of adsorbent particles is maintained at a specified temperature (Fig. 1a). As the fluid flows back and forth

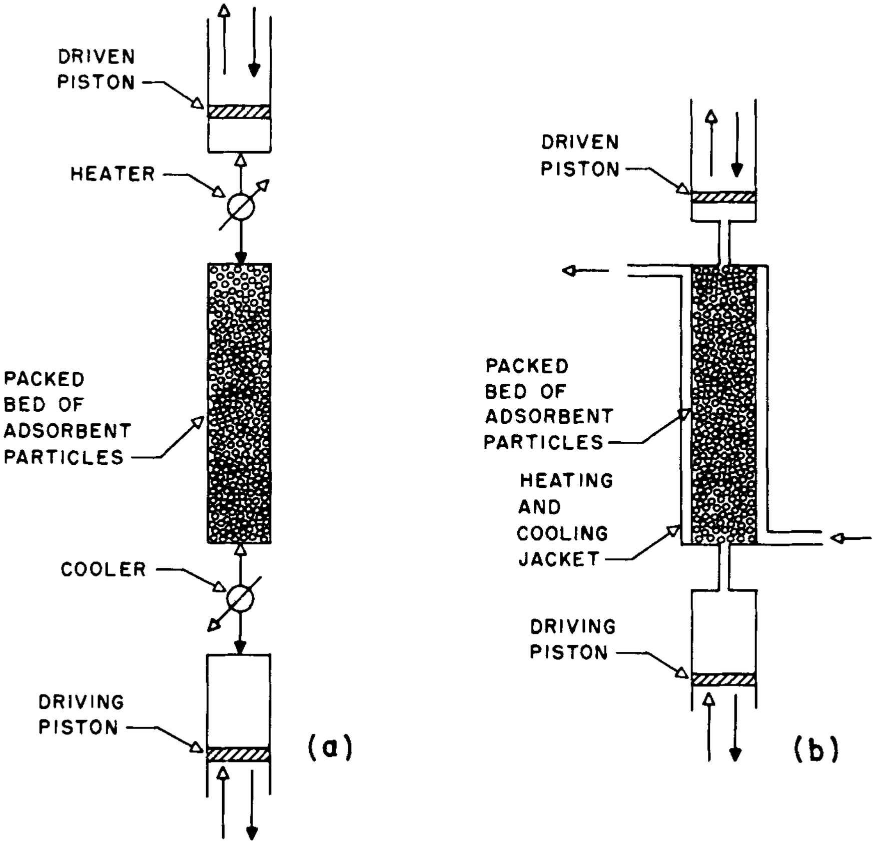

FIG. 1. Apparatus arrangement for thermal parametric pumping. (a) Recuperative mode. (b) Direct mode.

through the bed (from Requirement 3), it carries thermal energy into and out of the bed. At each axial position within the column the solid particles come into contact alternately with fluid coming from the hot end and with fluid from the cold end. In this way each particle experiences an alternating temperature field. The adsorption–desorption cycle produced by this field causes the alternating mass flux between particle and liquid phases (*4*).

The phase angle between the temperature and flow cycles is not uniform, but rather it varies with axial position depending on the flow rate and the thermal properties of the bed. It has been shown, however, that the best separations occur when these cycles are exactly in phase

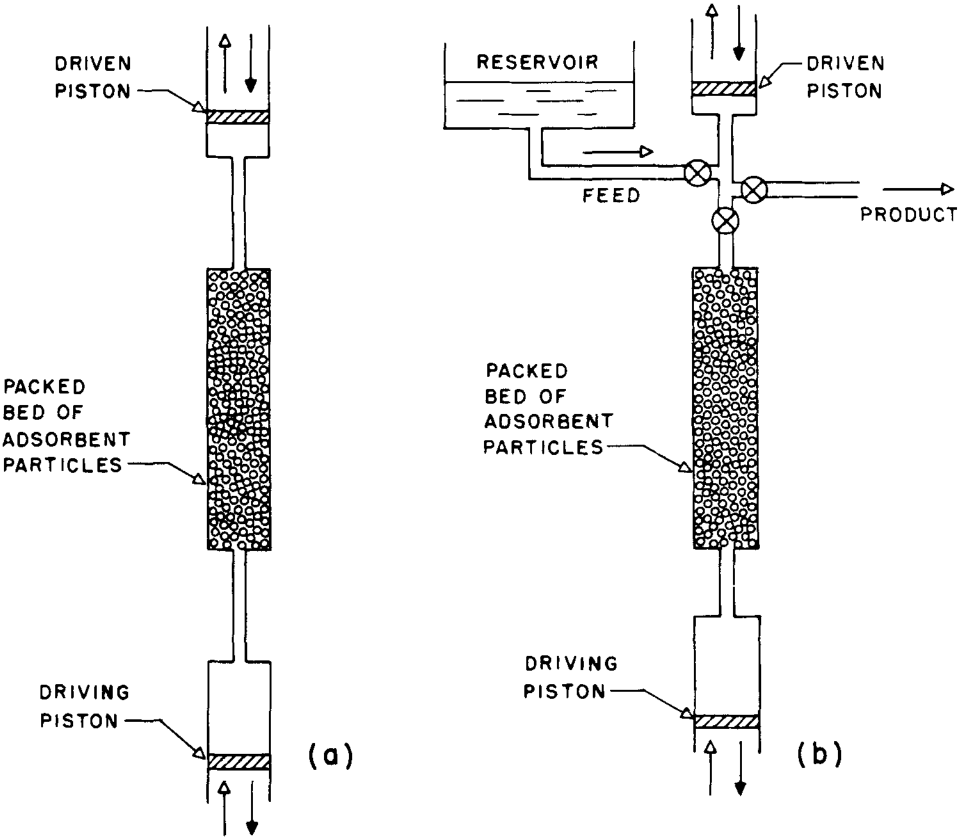

FIG. 2. Feed input and product removal for a generalized parapump column. (a) Batch operation. (b) Semibatch operation.

(*2*). Since the angles vary with position, they cannot all be in phase; hence the recuperative thermal mode is less than optimal.

This phase angle difficulty can be overcome by using the direct thermal mode shown in Fig. 1b. By surrounding the column with a heating and cooling jacket, temperatures can be changed at will, uniformly throughout the bed. The recuperative mode does have one advantage over the direct mode—it can be operated so that a substantial amount of heat can be recovered. In the direct mode, heating is far more irreversible. In both thermal modes, however, separation arises from the coupling of adsorption–desorption cycles with the reciprocating flow.

Before considering a specific pH system, let us examine several ways in which feed can be introduced and product removed from a parapump column. The column can be operated as a batch (Fig. 2a) with no feed input or product removal. We sometimes refer to a batch process as operation at "total reflux," in analogy with distillation. The products which accumulate in the reservoirs are removed when the run is terminated. Another variant is the semibatch operation (Fig. 2b) with both feed and product streams at one end of the column and "total reflux" at the other end. A separation is produced as in the batch case but eventually the transient dies away, the product stream concentration approaches that of the feed, and the total reflux end concentration reaches a steady value. The third possible variant is the "steady-state" or "open" operation, where there are at least two product streams in addition to the feed. Separation here can continue indefinitely as long as feed and energy are supplied.

pH PARAMETRIC PUMPING

pH alternations can cause equilibrium solute distributions in certain materials (e.g., ion exchange resins) to vary, and so produce an alternating interphase solute flux. This flux, when coupled with an alternating axial solution flow, results in a separation. In analogy with the thermal system, pH parametric pumping also has a direct and a recuperative mode.

To implement the direct pH mode, one needs a column whose walls are permeable to hydrogen ion. In this way a change in the pH of the liquid surrounding the column can influence the pH inside the bed. Such a column could be formed from a selective membrane, but transport through the membrane would significantly complicate matters. For this and experimental reasons we chose to study only the recuperative mode.

In the recuperative mode reservoirs at the column ends are maintained at two different pH values. As solution moves back and forth through the bed, ion exchange particles experience a lower pH when flow comes from the acidic end, and a higher pH when flow reverses.

Maintaining two levels of pH during an entire experiment presents some problems. Buffers are a possibility, but they compete with the ion exchange process and so are unacceptable. Titration to the desired value of pH with acid or base is a viable alternative, but this method too presents some problems. The addition of titrant solution disturbs the concentrations of all ions. Adding aqueous HCl, for example, dilutes the solution at the acid end of the column. If this dilution is large, it could overwhelm the parapumping separation. Although this diluting effect cannot be avoided, it can be minimized by sensitive pH control and the use of HCl solution of high concentration. Furthermore, if a "batch" system were run and both reservoirs were titrated, the volume increase would upset mechanical pumping action. Hence the "batch" system was rejected. Instead, the recuperative semibatch system was adopted for the studies. The feed solution is alkaline with constant pH. The total reflux end is acidic, with pH control by titration with acid.

The object of our experimental investigation is to determine whether this process does produce a separation as theory predicts; what influence cycle time (an important variable in thermal work) has on the separation factor, if any; how significant is the diluting effect of titration with acid; and what effect, if any, Na^+ and K^+ have on each other.

From the parametric pumping theory we would expect Na^+ and K^+ to accumulate at the acid, closed end of the column. When flow is from the closed to the open end, fluid rich in H^+ moves into the bed, replacing some of the alkali metal cations already fixed there, according to the reaction:

$$RM + H^+ = RH + M^+$$

where R represents resin phase. The acidic solution thus becomes more concentrated in M^+ (Na^+ and/or K^+).

On the next half cycle this more concentrated solution moves out of the bed and feed rich in HO^- comes in contact with the resin, displacing H^+ from it and fixing Na^+ and/or K^+ on the solid phase.

The neutralization that occurs in this step is in effect the chemical energy source for the system. Acid and base must be supplied continually to provide the energy for separation.

APPARATUS

A borosilicate glass column (30 × 1.1 cm i.d.) is packed with 30–50 mesh particles of IRC-84, a carboxylic polyacrylic resin (Rohm and Haas) (see Fig. 3). The resin was pretreated by washing it to remove fines and then equilibrating it with the alkaline feed. During the experiment liquid is pumped back and forth through the bed by a constant rate, infusion-withdrawal syringe pump controlled by a programmed cycle timer.

The syringe connected to the top of the column receives solution from a large feed reservoir; the syringe at the bottom receives fluid

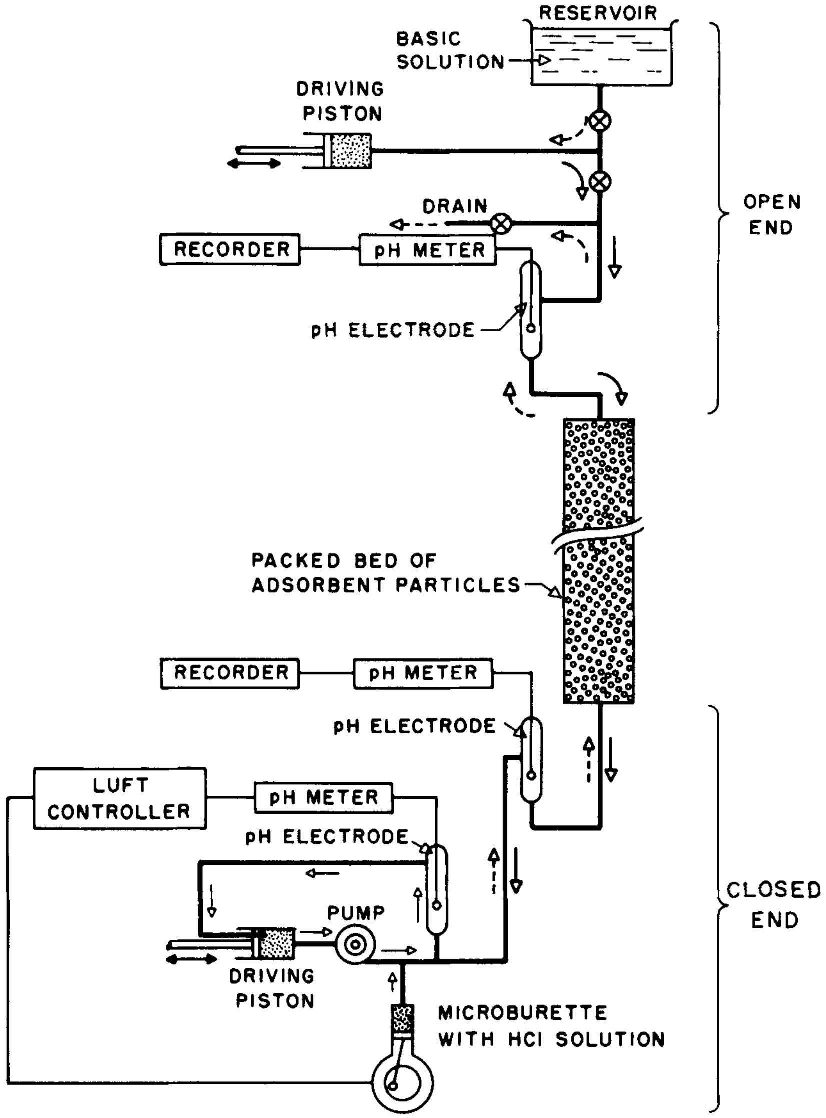

FIG. 3. pH parametric pumping apparatus.

from the column only. This bottom syringe is part of the mixing and control loop that makes up the closed (total reflux) end of the bed. The loop also contains a peristaltic pump, a combination micro-pH electrode connected to an expanded scale pH meter, a Luft on–off controller, and an automatic positive displacement, multi-speed, microburet that titrates the fluid to a pH 3.05 ± 0.05 end point. (To minimize the volume of acid titrant added, high concentration HCl solution was used.) A second pH electrode, situated just below the bed, measures effluent profiles; it is not part of the loop.

The circulation loop is essential for accurate pH control. Circulation rates are about 12 to 15 times greater than the column effluent rate.

EXPERIMENTAL PROCEDURE

The feed solutions used in these experiments were prepared from the chlorides and hydroxides of Na^+ and K^+ to pH = 11.75 ± 0.05 and the cation concentrations shown in Table 1. An experimental run begins with the resin in equilibrium with the feed at ambient temperature. The interstitial liquid in the bed is also of this feed composition. An

TABLE 1

Measured Cation Concentrations at the Total Reflux End

Run No.	Cycle time (min.)	Cycle No.	$[K^+]$ fluid (meq/ml)	$[Na^+]$ fluid (meq/ml)	$[K^+ + Na^+]$ fluid (meq/ml)	Separation factor	HCl solution titrant (ml)
1	16	0	0.100	0.100	0.200	1.00	3.85 (2.0 M)
		100	0.113	0.114	0.227	1.14	in 356 cycles
		350	0.116	0.116	0.232	1.16	
2	16	0	—	0.100	—	1.00	3.75 (2.0 M)
		100	—	0.140	—	1.40	in 370 cycles
		350	—	0.117	—	1.17	
3	16	0	0.100	—	—	1.00	7.00 (2.0 M)
		100	0.146	—	—	1.46	in 510 cycles
		350	0.117	—	—	1.17	
4	16	0	0.0500	0.0500	0.1000	1.00	5.90 (2.0 M)
		100	0.0617	0.0625	0.1242	1.24	in 449 cycles
		350	0.0657	0.0660	0.1317	1.31	
5	16	0	0.0200	0.0200	0.0400	1.00	1.50 (3.0 M)
		268	0.0200	0.0198	0.0398	0.99	in 268 cycles
6	45	0	0.100	0.100	0.200	1.00	1.50 (2.0 M)
		100	0.115	0.115	0.230	1.15	in 100 cycles
7	16	0	0.0500	0.0500	0.1000	1.00	2.40 (3.0 M)
		100	0.0634	0.0730	0.1364	1.36	in 553 cycles
		350	0.0852	0.0992	0.1844	1.84	

acidic solution (pH = 3.05 ± 0.05) with the same Na^+ and/or K^+ concentration as the feed is in the closed reservoir. The volume of solution is the closed end loop is 40 ml, of which 10 ml fills the syringe. At these values of pH, the uptake of H^+ by the week carboxylic resin is at, respectively, a minimum and a maximum (*5*, *6*).

The first half-cycle begins with feed moving downward from the top alkaline syringe. As feed enters the top of the bed, an equal volume of fluid leaves the bottom and enters the closed end loop where its pH is kept at 3.05 ± 0.05.* When 11.85 ml (approximately 1.4 times the bed interstitial volume) has been displaced downward, a programmed cycle timer causes the syringe pump to reverse direction, the circulation in the closed loop to stop, valves to switch, and upward flow to begin. The fluid leaving the top of the bed is analyzed and then discarded. Meanwhile the top syringe is refilled automatically from the feed reservoir. The closed loop is sampled (0.20 ml) at approximately 50 cycle intervals and analyzed for Na^+ and/or K^+ by flame spectrophotometry. An experimental run is continued until the closed end concentration becomes steady.

RESULTS AND DISCUSSION

Our experiments confirm the parapump theory. Cations, both Na^+ and K^+, do accumulate at the acid end of the column. Figure 4 shows the transient behavior of this closed end for seven different feed or operating conditions, with normalized concentrations of total cation content plotted vs number of cycles. Transient separations up to 84% concentration increase appear, in one instance, with long time concentrations of 20–30% above the feed in most cases. This concentration increase is in spite of the dilution effect of the acid used for pH control. In Run No. 4, for example, 4.8 ml of 2 *M* HCl was added to the closed end reservoir during 350 cycles and still the 40 ml of solution at that end was 30% more concentrated than the feed.

We found no significant difference between Na^+ and K^+ in Runs 1–4 and 6 in which the volume of HCl solution added was large due to less than optimal pH control. In Run 7, where the volume of titrant was only one-third as much as before, there is a difference between Na^+ and K^+ separations. In Table 1 the concentrations at the closed end reservoir are given for cycles 100 and 350 of each run only, to-

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* In runs 1, 2, 4, and 6, 2.0 *M* HCl solution was used in the microburet at a rate of 0.777 ml/min, and in run 3 at 0.103 ml/min. Run 5 used 3.0 *M* HCl at 0.020 ml/min and in run 7, 3.0 *M* HCl at 0.055 ml/min was used.

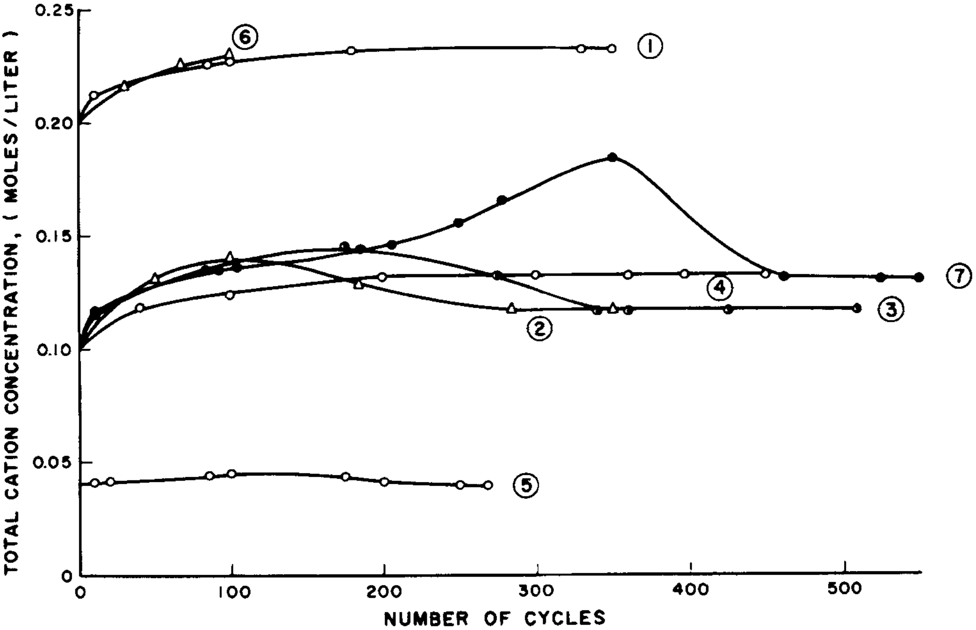

FIG. 4. Total cation concentration of the fluid phase measured at the total reflux end vs number of cycles for seven different operating conditions described in Table 1.

gether with the volume of HCl solution used. The importance of HCl molarity and the rate of infusion can be easily seen. Further studies on this point are underway.

There appears to be little effect of cycle time (runs Nos. 1 and 6, of 16 and 45 min, respectively) over the range of these experiments; this is due to the slow rate of mass transfer between the phases. For much longer or much shorter cycles, however, we would expect different behavior.

Total ion concentration in the feed does affect the separation: in the lowest total concentration run (No. 5), no separation was observed throughout the run because by using a too dilute solution we probably reached the point of electrolyte exclusion (7). Runs with Na^+ and/or K^+ concentrations of 0.1 *M* titrated with 2.0 *M* HCl (Nos. 1, 2, 3, and 6) all produced the same long-time separation of 1.16.

The intermediate concentration gave the greatest separations, and there appears to be an optimum total feed concentration near 0.10 *M*. No complete explanation can be made now without further study;

however, ionic concentration on the ion exchange equilibria certainly must affect the process.

CONCLUSION

A pH driven parametric pump has been developed to concentrate Na^+ and K^+ ions. With no attempt at optimization, separations of 1.2–1.8 were obtained in spite of the diluting effect of pH control.

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