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Yeshayahu Talmon[a]; Eliezer Rubin[a]
[a] Department of Chemical Engineering Technion, Israel Institute of Technology, Haifa, Israel

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Chromatographic Separation by Foam

YESHAYAHU TALMON and ELIEZER RUBIN

DEPARTMENT OF CHEMICAL ENGINEERING
TECHNION, ISRAEL INSTITUTE OF TECHNOLOGY
HAIFA, ISRAEL

Abstract

The development of a unique chromatographic separation method based on liquid foams is described. The sorption bed is liquid foam moving in a tall vertical column in plug flow manner. The foam is eluted from the top countercurrently to its motion. The mechanism of separation of mixtures is based on adsorption to bubble surface and/or utilizing the foam producing surfactant as a selective carrier. It is shown how this technique can be used for pulse as well as for continuous chromatographic separations. Results of some systematic studies on the effect of two independent variables, foam velocity and elution rate, on separation of mixtures of organic dyes is presented and discussed.

INTRODUCTION

In the classic method of chromatography a pulse of a mixture of dissolved substances is separated by the selective adsorption of its components on a fixed bed of sorbent, eluted with a liquid or a gas. This is a semibatch operation applicable usually for very small quantities of separated materials. Chromatography has developed into an excellent analytical tool.

Attempts to convert chromatography into a continuous process for large volume separations proved impractical because of the problems encountered in moving the solid bed in plug flow countercurrently to the eluting fluid. Thus the few fairly large chromatographic separators developed for industrial use utilize the same approach and principles of analyti-

cal fixed bed chromatography, i.e., pulse of a mixture and elution, but in large diameter columns.

The purpose of this paper is to present our ideas and experimental work on utilizing liquid foams as a sorbent bed for chromatographic-type separation.

Liquid foams have quite a large specific area for adsorption, and they can be easily made to move in a plug flow manner. Liquid foams are dispersions of gas in a relatively small amount of liquid. The bubbles of the gas are surrounded by thin films of liquid stabilized by adsorbed layers of surface-active solutes (surfactants). A foam can be generated by bubbling gas through a pool of a liquid solution of a surfactant. The foam collects above the solution. If this liquid pool is in the lower section of a vertical smooth pipe, the foam can be made to move upward in the pipe and be collected at the top. The size of the bubbles, their velocity, and the pattern of the flow of the foam can be controlled by the type of sparger and by the rate of the gas bubbled through the solution (*1*).

Foam columns as described above have been used in the foam fractionation method (*2–4*) in which one or more solutes are separated from the liquid pool because of their different affinity to the gas–liquid interface. Foam fractionation columns can also be operated continuously by continuous introduction of fresh feed into the liquid pool or directly into the foam (*2, 5, 6*).

The basic idea of the present work was to use these moving foam columns as moving sorbing beds. The components of a mixture of solutes injected into such a foam column may have affinity for the gas–liquid interface because of three main reasons: (a) they may be surface active and therefore tend to adsorb to the gas–liquid interface as does the foam-producing surfactant; (b) they may be electrostatically attracted to an oppositely charged foam-producing surfactant; and (c) they may form a complex with the foam-producing surfactant. In the last two possibilities the foam-producing surfactant acts essentially also as a carrier. By eluting the foam column from the top, the mixture of solutes injected into the foam should separate, with the solutes having a higher affinity for the gas–liquid interface being washed downward slower. This will result in a chromatographic-type separation of the solutes. Moreover, since foam can be easily moved continuously in plug flow (*1*), it should also be possible to continuously introduce feed and eluting solution and thus obtain a continuous chromatographic separation.

This paper presents a description of the development as well as experimental work with foam chromatographic columns. Described are pulse

and continuous separation experiments as well as results of studies on the effect of several important variables on extent and efficiency of separation.

DEVELOPING THE METHOD—PRELIMINARY EXPERIMENTS

The chromatographic foam separation method was developed step by step from the basic idea to the operating system. A short description of the preliminary experiments will clarify the reasons for the final selection of mode of operation and experimental system described in the next section. In order to facilitate qualitative observations and quantitative analysis, the separation was tested on sets of pairs of organic dyes. These dyes, such as crystal violet, methylene blue, and Congo red, are easy to handle, easy to observe and follow in the foam column, and easy to analyze spectrophotometrically.

In the first set of preliminary experiments, air was bubbled through a surfactant solution located at the bottom of a vertical glass column. When the foam reached the top of the column, the gas bubbling was stopped and a mixture of dyes was injected as a pulse into the static foam column at the column top. Eluting solution, containing the same surfactant used for producing the foam column, was introduced from the top. It was found that each dye had a different decending velocity and therefore a different elution time, as found in chromatography with solid sorbents. These simple experiments helped to choose convenient sets of dyes to work with in subsequent experiments. The static foam column experiments suffered, however, in that the foam tended to collapse with time. It was concluded, therefore, that this mode of operation is not practical.

In the second set of preliminary experiments the foam was continuously produced, and a sample of dyes was injected as a pulse into the moving (dynamic) foam eluted from the top countercurrently to the moving foam with the foam-producing surfactant solution. The eluted liquid was collected and removed from the liquid pool at the bottom, through which air was continuously bubbled to generate the foam. The foam was collected continuously from the top and collapsed. When a solution of differently charged dyes was injected into the foam of negatively charged sodium dodecylbenzene sulfonate (NaDBs), separation was observed: the positively charged dye moved upward while most of the negatively charged dye was carried downward with the eluting solution. Similar good separations were obtained when one of the dyes injected formed a complex with the surfactant whereas the other dyes had no affinity for it. Under proper operating condition no problems with foam stability were encountered.

These results led to the final set of preliminary experiments, i.e., continuous introduction of a feed consisting of a mixture of dyes into the continuously moving foam column. By careful regulation of operating variables, i.e., foam velocity, feed flow rate, and elution rate, it was possible to separate the dyes so that one dye left continuously with the foam through the top of the column and the other dye left with the bottom stream from the liquid pool.

With these results demonstrating and proving the general idea, the experimental technique was further improved and systematic studies were then conducted on the effect of foam velocity and elution rate on extent of separation in pulse experiments and capacity of the continuously operated column.

EXPERIMENTAL

The final experimental system design enabled us to carry out both pulse and continuous experiments in the same system with only slight modifications. The general experimental system is depicted schematically in Fig. 1. The column itself is shown in Fig. 2.

The all-glass foam column (17) had an inside diameter of 38.5 mm. It was equipped with several small diameter side arms (27) which enabled us to inject the feed dye mixture at different locations if desired. The feed was introduced through a bent hypodermic needle which was usually located about halfway between the liquid pool and the foam exit. The length of the zone between the tip of the eluting tube and foam exit (A in Fig. 2) was kept at 15 cm. It was found that under our experimental conditions this length sufficed to assure maximum drainage of the foam and obtaining constant foamate rate at a given foam velocity. Increasing this length did not change the wetness of the exiting foam, whereas reducing it to below about 10 cm resulted in increasing foam wetness.

Surfactant solution for elution was introduced from tank (2) into the top of the foam column (20) through rotameters and a needle valve. Humidified nitrogen was introduced into the foam column (17) through a spinnerette. The platinum spinnerette (manufactured by Engelhard Industries Ltd.) had 50 holes, 0.04 mm each, and was installed in a stainless steel spinnerette holder (15). The use of a spinnerette resulted in uniform bubble size distribution which was found beneficial in operating the foam column. Liquid, originating primarily from eluting at the top, was removed at the bottom through a flexible tube (23) which was also used for regulating the height of the liquid pool (16). The top of the column was sealed

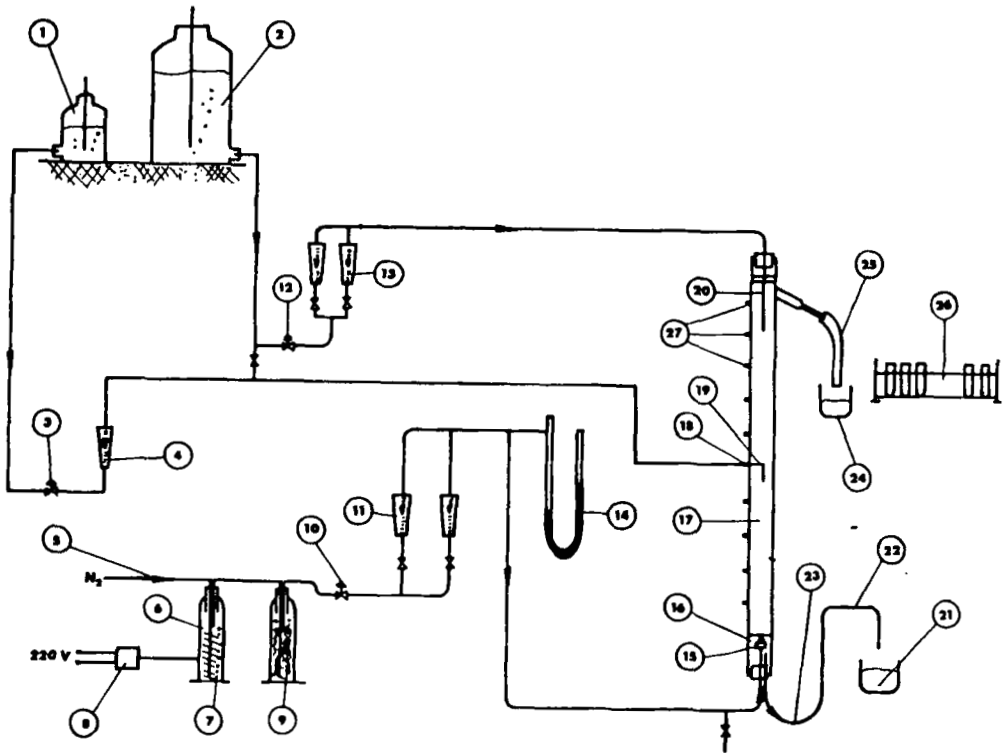


FIG. 1. Schematic diagram of the experimental system. (1) Dye solution feed tank. (2) Surfactant solution feed tank. (3) Needle valve. (4) Rotameters. (5) Nitrogen line. (6) Nitrogen saturation with water vapors. (7) Heating tape. (8) Temperature control in heating tape. (9) Droplets trap. (10) Needle valve. (11) Rotameters. (12) Needle valve. (13) Rotameters. (14) Manometer. (15) Spinnerette and spinnerette-holder. (16) Liquid pool. (17) Foam column. (18) Adapter. (19) Injection needle. (20) Elution tube. (21) Bottom collection container. (22) Opening to atmosphere. (23) Liquid pool liquid level regulation. (24) Foamate collection. (25) Foamate outlet tube. (26) Fraction collector. (27) Alternative openings.

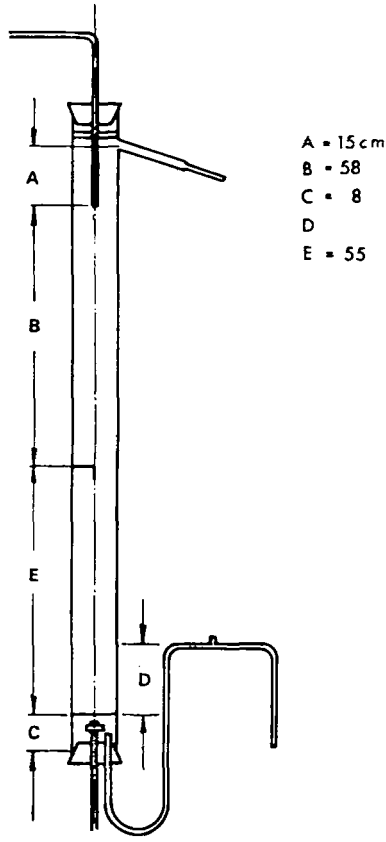


FIG. 2. Schematic representation of the column. Typical lengths are shown.

with two rubber stoppers through which the eluting solution was introduced. The foam left the top of the column through exit (25) connected to a flexible tube with which it was possible to direct it into test tubes or small beakers which contained small amounts of acetone that caused the foam to collapse. The dye mixture, introduced through hypodermic needle (19), was injected in pulse experiments by a micrometric syringe. In continuous experiments it was fed to the column from reservoir (1) through a needle valve (3), a rotameter (4), an adapter (18), and the same hypodermic needle.

The concentration of dyes in the collapsed foam liquid (foamate), C_i,

was determined by collecting it in a test tube with acetone, as mentioned above, for a measured period of time. The contents of the test tubes were diluted into a known volume of acetone and the absorbance of the solution was measured in a double beam spectrophotometer. From knowledge of the foamate flow rate and specific absorbance, the concentration could be determined. The foamate flow rate, q, was determined by measuring the time required to collect a given volume of foam using a specially designed container. Since foam moved in plug flow regime in all experiments, the foam flow rate could be calculated by following the velocity of a single bubble along the foam column wall, or from the nitrogen flow rate. The wetness of the exiting foam, ε_t, was calculated from $\varepsilon_t = q/vA$. The average wetness of foam in the column, $\bar{\varepsilon}$ (in Regions E and B, Fig. 2), was determined by stopping the column operation and measuring the increase in liquid pool level after all the foam collapsed (appropriate corrections for Regions A and C were made).

Before any dyes were injected the foam column was brought to steady-state operation and the various properties of the foam were measured. These included the foamate flow rate and the concentration of the surfactant in the foamate and the liquid pool. The foam bubbles were photographed in different locations along the column. From the enlarged pictures the average bubble diameter could be determined. Average bubble diameter was around 0.7 mm.

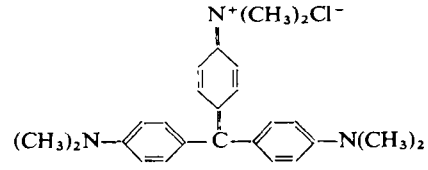
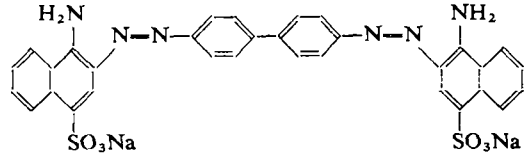
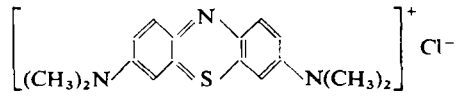
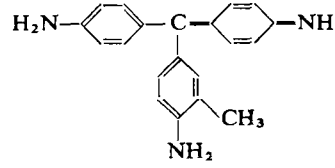
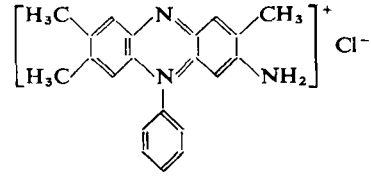
The surfactant used in most experiments was NaDBS. Its concentration was 10^{-3} mole/l just below its critical micelle concentration ($\sim 1.15 \times 10^{-3}$ M according to our findings). Accurate NaDBS concentrations in various streams were determined spectrophotometrically in the UV range at 222 or 258 mμ.

Elution rates were between 5 and 22 cm^3/min. A few runs were carried out with no elution. In these experiments the surfactant solution had to be introduced directly into the liquid pool in order to avoid depletion of the surfactant in continuous operation of the foam column. Foam velocities ranged between 2 and 10 cm/min. In pulse experiments the pulses contained 2.5×10^{-4} M of both dyes (usually a mixture of only two dyes was used) prepared by dilution of 10^{-3} M solutions of the dyes in the elution solution. This was done in order to avoid breaking of the foam while injecting the mixture. The volume of pulses was 1.0 cm^3, and they were injected in 10 sec. In the continuous experiments the flow rate of the dye solution was between 0.25 and 0.86 cm^3/min, and the dye concentrations ranged from 1×10^{-5} to 2×10^{-4} M. In continuous feed experiments the dye solutions were also prepared by dilution in surfactant solution.

In pulse experiments the "elution curve" (concentration of dyes in foamate vs time from injection) was determined. Note that these curves represent concentrations measured in the foamate. This is somewhat different from regular fixed bed chromatography, because foamate leaves at the same side of the column where eluting liquid is introduced. This difference stems from the fact that the foam is constantly moving. Concentrations in the diluted bottom outlet were usually not measured.

In the continuous experiments the system was brought to steady-state operation characterized by no changes in the dependent variables of the system. The dye concentrations were then determined in the foamate, from which the recovery of dyes could be calculated.

TABLE 1
List of Organic Solutes Used

(A)	Crystal violet: Positively charged, weak surface activity	
(B)	Congo red: Negatively charged	
(C)	Methylene blue: Positively charged, forms a complex with NaDBS	
(D)	Fuchsine	
(E)	Safranin: Positively charged, weak surface activity	

Dyes were inejected or fed into the column in pairs. The dyes used in almost all experiments are listed in Table 1. A few experiments were also conducted with three other dyes: toluidine blue, trypan blue, and Janus green. Experimental results with these dyes are not reported here because of the preliminary nature of the experiments.

RESULTS AND DISCUSSION

Three modes of operation were investigated quantitatively: pulse injection of dye mixtures without elution, pulse injection of dye mixtures with elution, and continuous feeding of dye mixtures with elution. In all cases the foam was dynamic, i.e., continuously produced by bubbling nitrogen into the liquid pool, and its motion was in the plug flow regime.

From the preliminary experiments as well as from preliminary attempts to analyze theoretically the chromatographic separation by foams, it was clear that the number of independent variables associated with each mode of operation is very large. It was decided, therefore, that in the present work the effect of two variables on separation would be studied: foam velocity, v (or equivalently flow rate per unit cross section), and elution rate, Q. Prior to studies of these two variables and their effect on separation of dye mixtures, several experiments were conducted in order to determine the foam properties as a function of design and operation parameters. In particular, it was important to determine the minimum length of the drainage zone above the point of introducing the eluting solution (length A in Fig. 2). Typical experimental results of foamate flow rate, q, and NaDBS concentration in the foamate, C_F, as a function of drainage zone length, L_A, are shown in Fig. 3. This figure indicates that above a drainage zone length of about 12 cm, foamate flow rate and NaDBS concentration in the foamate are constant. A similar conclusion is arrived at when using other elution rates within our experimental range. Therefore, a drainage zone length of 15 cm was used in most experiments. At this length the foamate flow rate, q, average wetness of exiting foam ε_t, and NaDBS concentration in the foamate depend only on foam velocity. Note that the average wetness of the foam in the column, $\bar{\varepsilon}$, depends in all cases both on foam velocity and elution rate.

Pulse Experiments Without Elution

In order to examine the importance of elution, experiments were first conducted without elution. In order to avoid surfactant depletion and

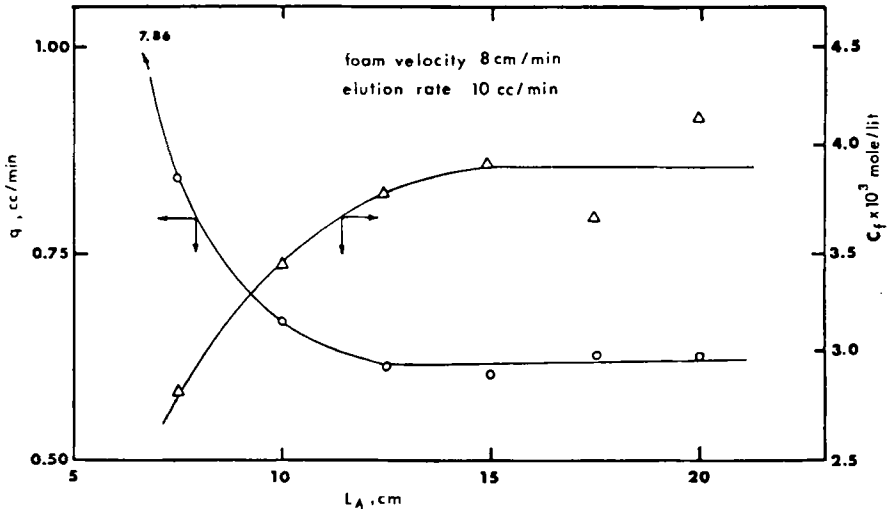


FIG. 3. Foam properties vs drainage zone length.

foam instability, it was necessary in these experiments to replenish continuously the surfactant concentration in the liquid pool by continuously feeding it with NaDBS solution. Although no elution was used, some elution effect is obtained from the liquid solution of the pulse (1 cm^3 in volume) draining through the foam.

Figure 4 shows foamate concentration vs time for a mixture of crystal violet (CV) and Congo red (CR). During this experiment it was observed that right after injection a dark-colored spot moved upward in the moving foam. This spot separated slowly into two bands moving slowly upward in the foam. Only little spreading of the CV band was observed, whereas the CR band spread out much more. From Fig. 4 it can be seen that complete separation of the two bands was obtained at the foam column exit. Recovery of the two dyes in the foamate was complete.

Results of a similar experiment with methylene blue (MB) and fuchsine are shown in Fig. 5. It is clear that for this system of dyes, separation is poor although a longer residence time in the foam column was used (foam velocity of only 3 cm/min).

The differences in the separations demonstrated by Figs. 4 and 5 are due to the differences in affinity of the different dyes for the gas–liquid interface. CV is positively charged whereas CR is negatively charged.

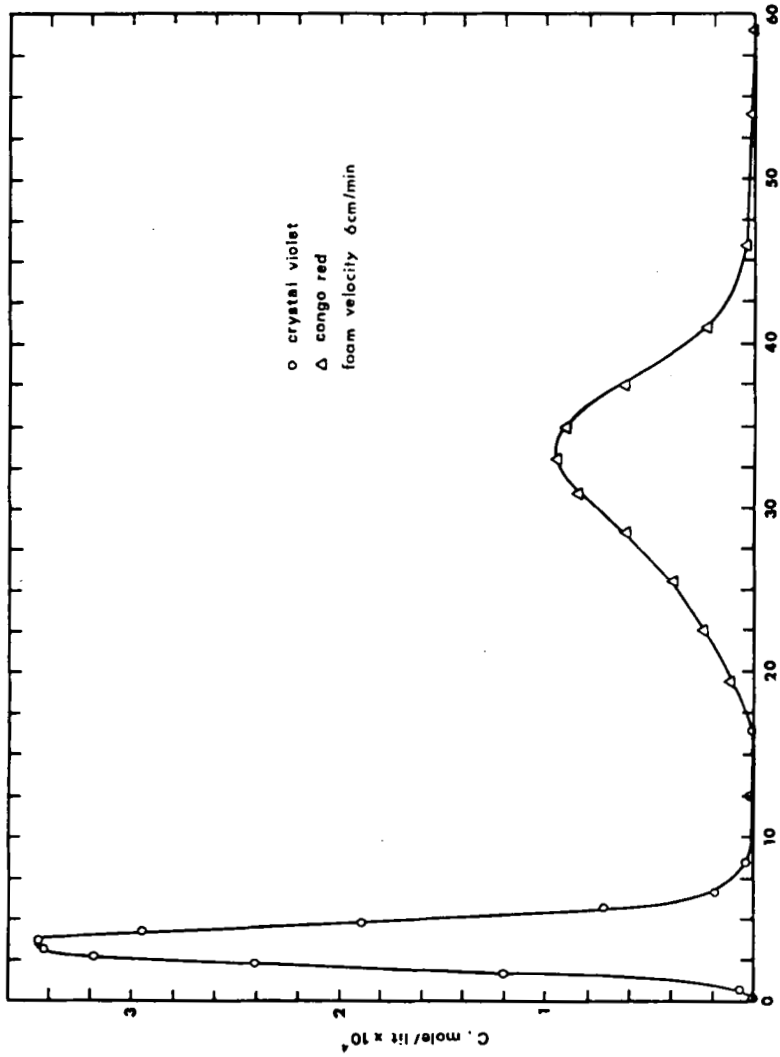


FIG. 4. Crystal violet and Congo red concentration in foamate as a function of time. Pulse experiment without elution. (○) Crystal violet (CV). (△) Congo red (CR). $t = 0$ indicates appearance of first trace of color in foamate.

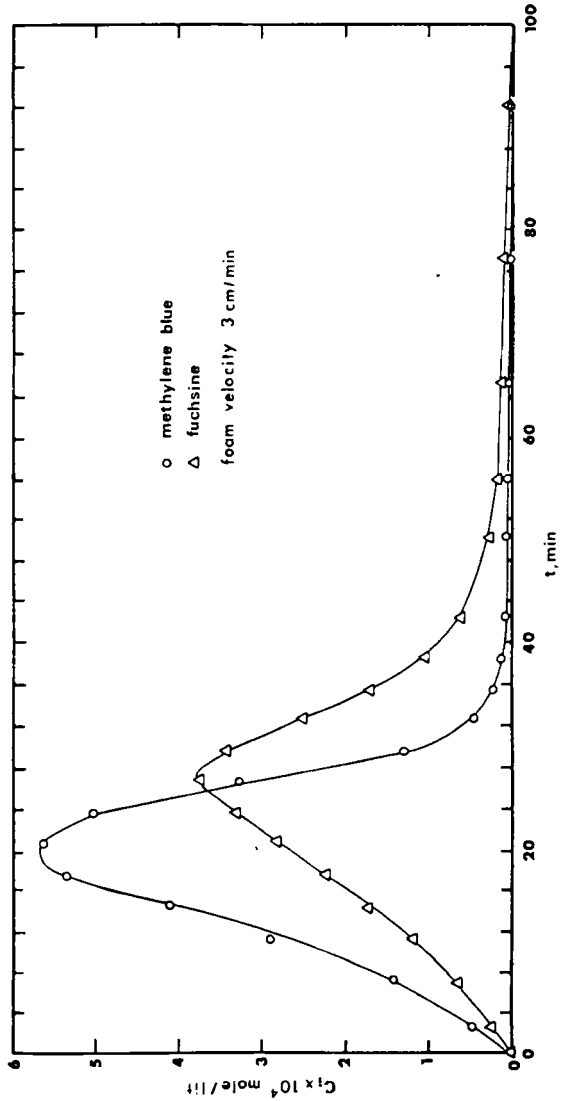


FIG. 5. Methylene blue and fuchsine concentration in foamate as a function of time. Pulse experiment without elution. (○) Methylene blue (MB). (△) Fuchsine. $t = 0$ indicates appearance of first trace of color in foamate.

Thus CV has a strong affinity for the negatively charged monolayer of the adsorbed NaDBS at the gas–liquid interface. CR has no affinity for the gas–liquid interface. Consequently, good separation between these two dyes can be expected and indeed was also obtained.

In the case of MB and fuchsine, MB forms a complex with NaDBS. (As a matter of fact, this strong tendency for complex formation is utilized for analysis of sulfonated surfactants.) The affinity of fuchsine for the gas–liquid interface is also strong. The result is therefore poor separation between these two dyes, at least when no elution is used.

The higher concentration of the peaks in Fig. 5 relative to Fig. 4 stems from the dryer foam obtained at the lower foam velocity used with MB and fuchsine.

Pulse Experiments With Elution

In general it was found, as expected, that elution can improve considerably the separation between the dyes injected. For convenience in the present work and in order to examine and demonstrate the separation between pairs of dyes having different affinity for the gas–liquid interface, three pairs of dyes were examined.

The first pair, CV and CR, is typified by the positively charged CV and negatively charged CR and should yield excellent separations with negatively charged NaDBS foam. Figure 6(A) shows the results of a pulse experiment with this system, using even a higher foam velocity than in Fig. 4 but with elution. All the CR was washed off into the bottom stream, and the foamate analysis indicates a 100% recovery and a fairly sharp CV peak.

The second pair, MB and fuchsine, is typified by complex formation between MB and NaDBS, i.e., strong affinity to the gas–liquid interface, and the moderate affinity of fuchsine. Figure 6(B) shows the results of pulse experiments with this system, using the same foam velocity as in Fig. 5 but with elution. It is clear, by comparing Figs. 5 and 6(B), that elution improves separation although partial overlapping exists. For the experiment in Fig. 6(B), 100% recovery of MB was obtained in the foamate whereas part of the fuchsine was washed into the bottom stream.

The third pair, MB and safranin, is typified by the strong affinity of both dyes for the gas–liquid interface: Complex formation between MB and NaDBS, and positively charged safranin. Figure 7 shows that the results of pulse experiments indicate poor separation between the dyes.

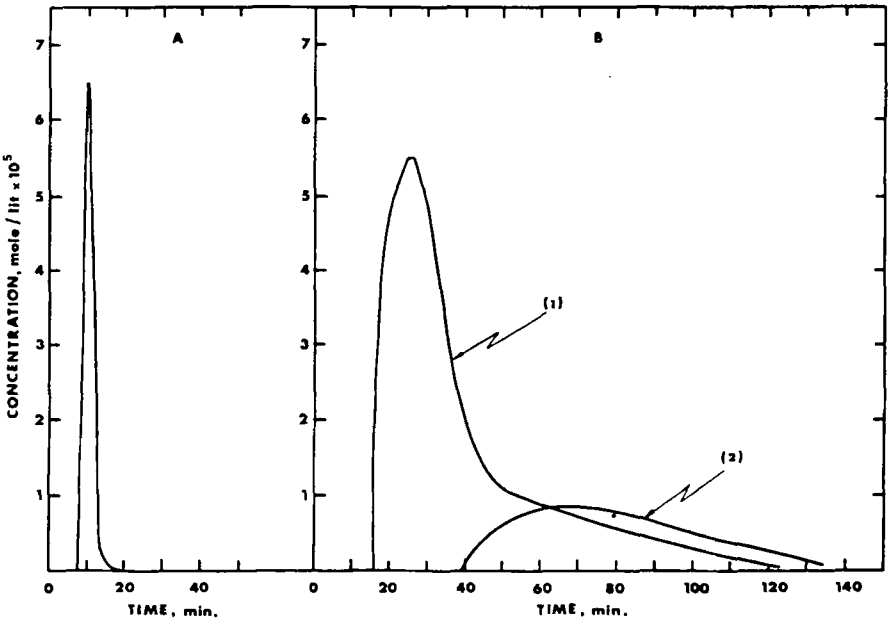


FIG. 6. Dye concentration in foamate. Experiments with elution (elution curves). (A) CV and CR. Curves are for CV. CR was completely washed down. Foam velocity 10 cm/min, elution rate 5 cm^3/min. (B) MB and fuchsine. (1) MB, (2) fuchsine. Foam velocity 3 cm/min, elution rate 9.5 cm^3/min.

Both dyes were practically 100% recovered in the foamate (MB 100%, safranin 95%).

Results of systematic studies on the effect of elution rate and foam velocity on concentration in the collapsed foam (elution curves) from the time of pulse injection for the system CV and CR are shown in Figs. 8 and 9. For this system CR was carried down completely into the bottom liquid. Figure 8 indicates that at a given foam velocity the time of appearance of the front of the CV, as well as the peak of the elution curve, are practically independent of elution rate. The time of appearance of the first trace of CV in the foamate at column exit is almost equal to foam height (A + B in Fig. 2) divided by foam velocity. Increasing the elution rate does, however, cause an increase in axial dispersion. This behavior of the positively charged CV, when using negatively charged foam-producing surfactant, is expected to be typical of solutes having strong affinity for the

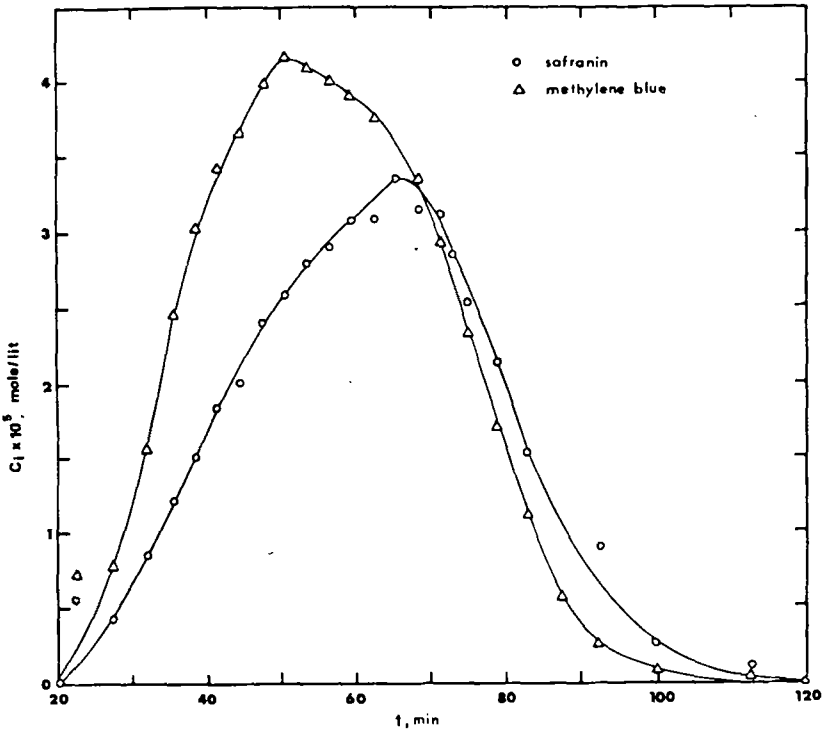


FIG. 7. Safranin and MB concentration in foamate. Pulse experiment with elution. (○) Safranin. (△) Methylene blue. Foam velocity 3 cm/min, elution rate 10 cm^3/min.

surfactant carrier. From Figs. 8 and 9 it is also evident that the appearance of the peak at the column exit is almost directly related to foam velocity and is almost independent of elution rate.

Figure 9 indicates that decreasing foam velocity has two effects: higher concentrations in the foamate and increased dispersion. The first effect is due to reduction in the foam wetness at column exit, ε_t, with decrease of foam velocity. Table 2 indicates that if peaks at different foam velocities are compared on the basis of CV molar flow rate, the molar flow rate increases with increasing foam velocity. This reflects the increase in dispersion as foam velocity is reduced, or equivalently as residence time is increased.

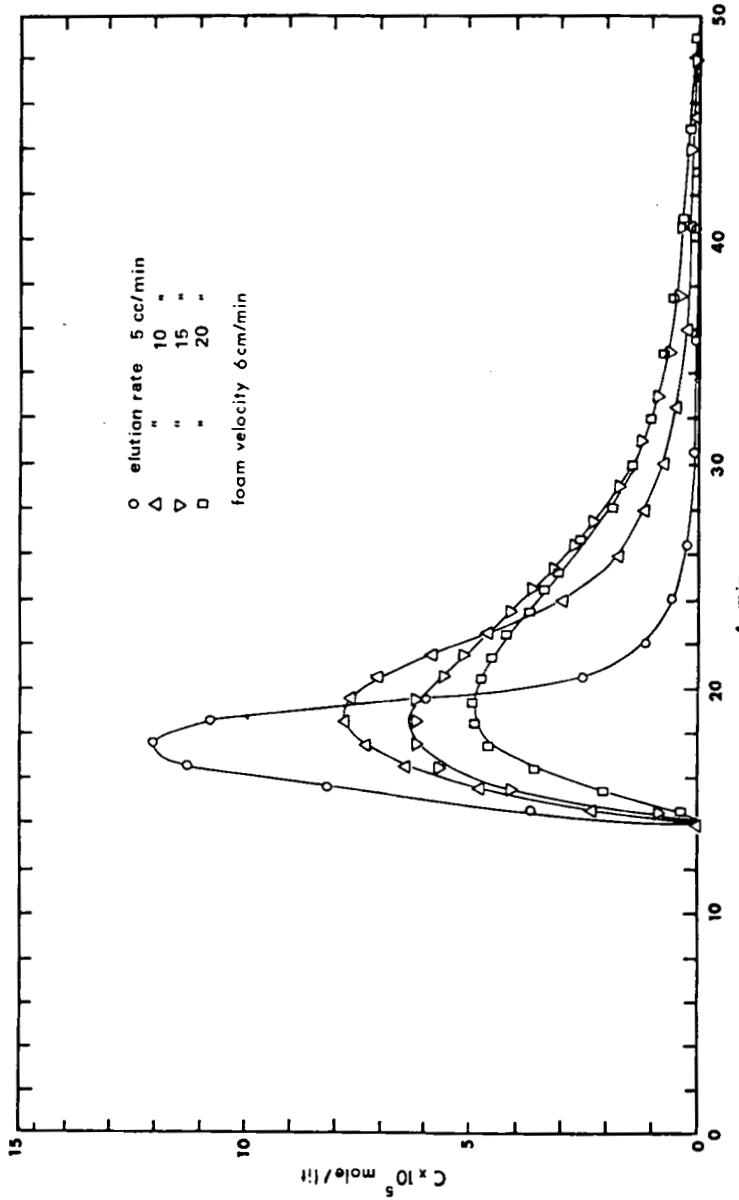


FIG. 8. CV concentration in foamate in pulse separation experiments (fixed foam velocity).

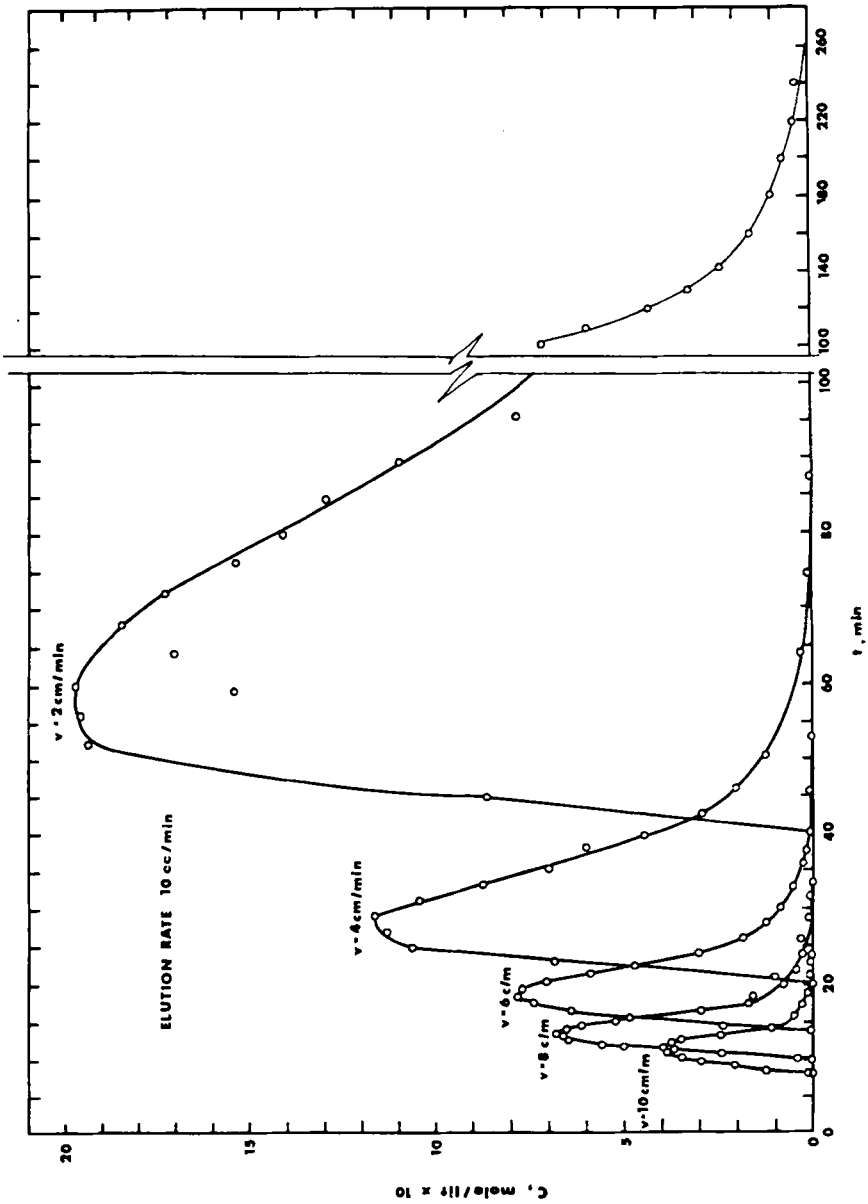


FIG. 9. CV concentration in foamate in pulse separation experiments (fixed elution rate).

TABLE 2

Maximal Molar Dye Rates in Foamate in Pulse Experiment (elution rate, 10 cc/min)

Expt. no.	Foam velocity v (cm/min)	Foamate rate q (cc/min)	Maximal dye conc. in foamate (moles/l $\times 10^5$)	Maximal molar dye rate in foamate (moles/min $\times 10^8$)
C-35	2	0.016	19.6	0.31
C-26	4	0.111	11.8	1.31
C-34	4	0.293	7.8	2.29
C-33	8	0.560	6.8	3.81
C-30	10	1.060	4.2	4.45

Increased elution rate, as well as a decrease in foam velocity and an increase in dispersion, are necessary for improved separation between dyes.

A few experiments were conducted with Triton X-100 (Rohm & Haas) as a foam-producing surfactant. This surfactant is nonionic. Pulses of mixtures of CV and CR which separated well with the anionic NaDBS foam were quickly washed down with Triton X-100 foam, giving no separation. This indicates that electrical charge effects were the main factor in separation of these two dyes with NaDBS.

Continuous Experiments

The first few continuous feed experiments conducted with the system CV and CR indicated that complete separation between these two dyes can be obtained: CV appears in the foamate whereas CR is washed down into the bottoms.

It was then decided to study the effect of foam velocity and elution rate on the maximal molar feed rate possible with maximum yield. Using a ratio of 1:1 of CV to CR, the total molar concentration of dyes in the feed was changed at a given set of foam velocity and elution rate conditions. For each feed concentration the CV recovery in the foamate was determined. A plot of typical results for foam velocity of 4 cm/min and elution rate of 10 cm^3/min is shown in Fig. 10. Note that each experimental point in this figure represents the result of a continuous steady-state experiment.

Figure 10 indicates that at the given foam velocity and elution rate about 80% of the CV is recovered in the foamate up to a molar feed rate of dyes of about 1.6×10^{-8} mole/min. The other 20%, as well as all the CR, is washed down continuously into the bottom stream. Above a molar

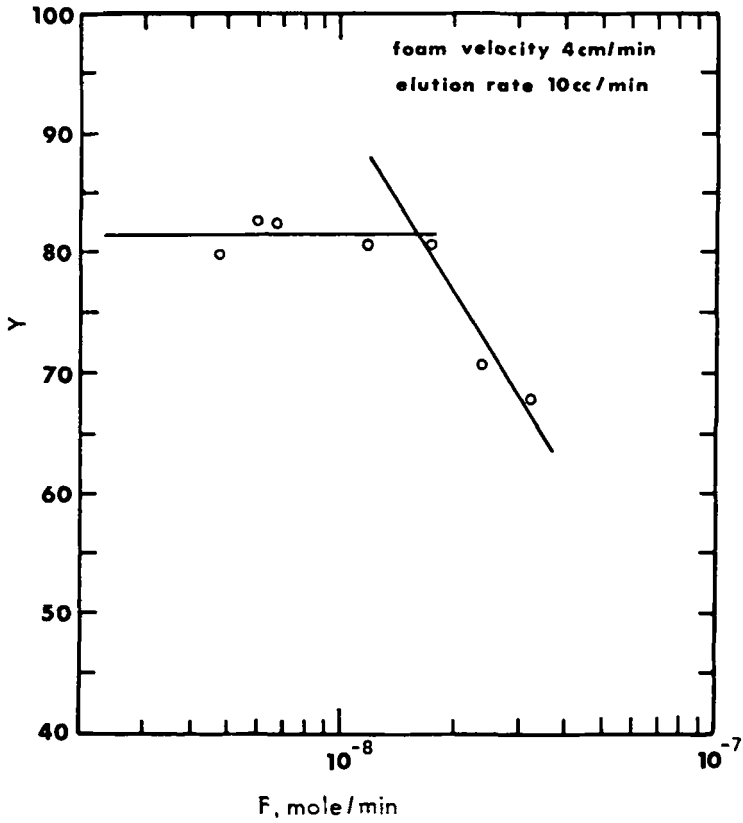


FIG. 10. CV recovery in foamate as a function of feed rate (continuous feed). Recovery in foamate, Y, refers to CV.

feed rate of about 1.6×10^{-8} mole/min the CV recovery in the foamate drops rapidly. Thus, at the given foam velocity and elution rate, 1.6×10^{-8} mole/min is the maximum molar feed rate F_m, at which the maximum recovery of CV can still be obtained. This value may also be considered as the optimum feed rate at the given foam velocity and elution rate.

The results of similar sets of experiments are summarized in Table 3. Using these results an attempt was made to find a general correlation between F_m and foam velocity, v, elution rate, Q, and average foam wetness in foam column $\bar{\varepsilon}$. The final general correlation is shown in Fig. 11.

TABLE 3

Maximal Dye Rate vs Foam Velocity and Elution Rate (system: CV and CR)

Expt. no.	Foam velocity v (cm/min)	Elution rate Q (cm^2/min)	Maximal dye rate F_m ($\times 10^8$ moles/min)	$\bar{\epsilon} \times 10^2$	Percent recovery of CV	$\frac{v^{1.68}}{\bar{\epsilon}^{0.75} Q^{0.25}}$
1	2	10	0.8	8.36	~60	11.59
2	4	10	1.6	8.36	85	37.14
3	6	10	3.1	8.36	100	73.39
4	6	5	7.0	6.39	100	106.76
5	6	15	2.6	10.19	75	57.17
6	6	20	2.0	12.16	80	46.59
7	8	10	6.0	8.36	95	119.00
8	10	10	7.0	8.36	100	173.12

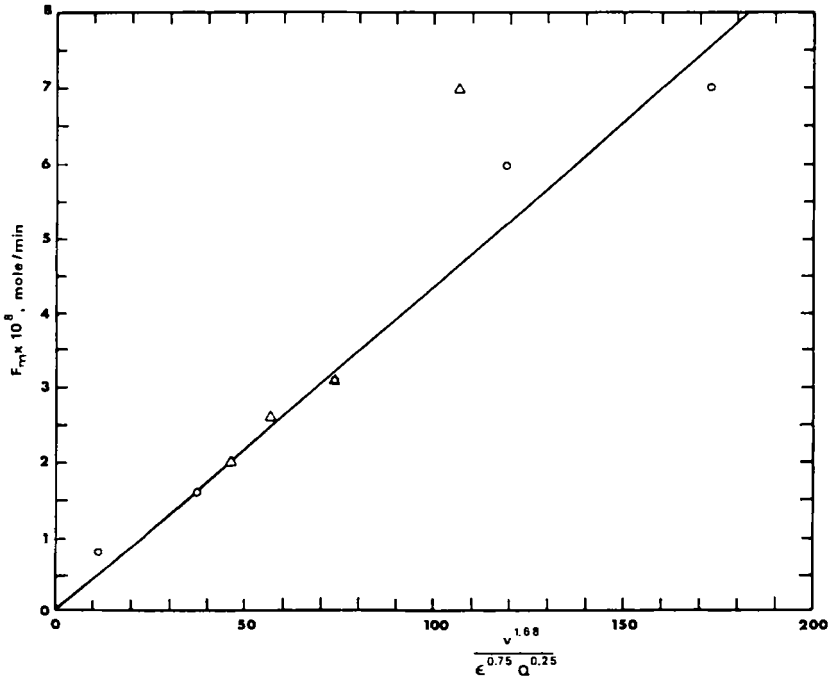


FIG. 11. Maximal dye rate vs foam velocity and elution rate.

This correlation indicates that F_m depends much more on foam velocity than on elution rate. Using a correlation such as Fig. 11 it is possible to determine for each molar feed rate the optimal relation between foam velocity and elution rate. Moreover, from Table 3 it can be seen that when $v^{1.68}/Q^{0.25}\bar{\varepsilon}^{0.75}$ is larger than about 70, recoveries of about 100% CV are obtained. Considerably lower recoveries are obtained at the lower values of this parameter. These results tend to indicate that it is beneficial to operate at higher foam velocities and lower elution rates. However, at the present state of the art it is difficult, if not impossible, to arrive at too extreme conclusions. Thus, when foam velocity is too high, backmixing may occur in the foam (*1*), which is detrimental to the chromatographic effect. When elution rate is too low, poor separation between the dyes may be expected.

CONCLUDING REMARKS

This paper presents the idea and describes the technique, equipment development, and methods of operation of dynamic foam columns for chromatographic separation of solute mixtures. The technique is shown to be applicable for pulse as well as continuous operation modes. The latter seems to be particularly attractive for potential larger scale operations involving separation of difficult to separate and expensive solutes.

The selection of a proper foam-producing carrier surfactant is the key to the separation of a given mixture of solutes. In our experiments the main mechanisms for separation between solutes were electrical charge and formation of a complex with the foam-producing surfactant.

Quantitatively, the experimental data demonstrate what separations have been accomplished in this early stage of the development and testing of the technique, and the effect of a few important variables on the extent and effectiveness of the separation.

Quite a few factors and variables, as well as additional operating techniques, have yet to be studied. Several pertinent possibilities and directions are worth mentioning.

The results of the present work were obtained with dyes—chemicals which are only fairly complex in structure and which are characterized by absorbance in the visible light. It will be interesting and instructive to examine the separation of complex, difficult to separate chemicals, such as enzymes and alkaloids.

The pulse experiments with our systems of solutes demonstrate increased axial dispersion with increasing elution rate and decreasing foam velocity

when elution is continued throughout the experimental period. Since the foam is moving and eventually collapses, it is not necessary to elute until solutes leave the foam column. It may be advantageous in certain cases to elute only for a short time after the pulse injection. This will most probably decrease considerably the axial dispersion. Since the chromatographic technique involves countercurrent motion of foam relative to eluting solution and collection and analysis of the foamate, this will also result in the appearance of all the solutes in the foamate. Thus, for example, for the system CV + CR, the CR will not be washed downward completely, but rather will appear as a peak after the CV, and the CV peak will be sharper.

The effect of additional variables as well as wider ranges of the variables already examined have to be studied experimentally.

We have not yet touched on the recovery of the desired products from the surfactant-containing foamate. The main problem is the presence of the foam-producing surfactant. Each case may require a different approach. Removal of surfactant from the foamate may be accomplished by simple means such as pH and temperature changes. Thus, for example, NaDBS changes into the difficulty soluble acid form when the pH is dropped to below about 6.0.

Finally, appropriate theoretical analysis of the pulse and continuous chromatographic separation by foams has yet to be developed. The theoretical derivations can be based on existing models and approaches for fixed-bed chromatographic separation. However, the motion as well as the unique properties and behavior of foams have to be properly incorporated into the equations.

Work is now in progress in some of the above-mentioned directions.

SYMBOLS

A	cross section area of foam column, cm^2
C_F	concentration of surfactant in foamate, moles/l
C_i	concentration of dye in foamate, moles/l
F	molar flow rate of dye solutes in feed, moles/min
F_m	maximal molar flow rate of dye solution feed, moles/min
L_A	drainage zone length, cm
q	foamate flow rate, cm^3/min
Q	elution rate, cm^3/min
t	time (usually starting at injection of pulse), min
v	foam velocity, cm/min

Y percent recovery in foamate
$\bar{\varepsilon}$ average liquid content in foam column, cm^3 liquid/cm^3 foam
ε_t liquid content of exiting foam, cm^3 liquid/cm^3 foam

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