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Improving Elution and Displacement Ion-Exchange Chromatography by Adjusting Eluent and Displacer Affinities

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Abstract

Multicomponent interference in ion-exchange chromatography is examined in this paper. A multicomponent chromatography theory is used to analyze the effect of eluent affinity in elution chromatography, and displacer and presaturant affinity in displacement chromatography. The eluent should have an affinity between those of the feed components and near the strongest affinity species. In displacement chromatography, the displacer and presaturant affinities should bracket those of the desired products as closely as possible. Displacement chromatography produces pure product peaks, although the feed throughput is larger for elution chromatography. These conclusions are also valid for adsorption chromatography.

Ion-exchange and adsorption chromatography have gained in popularity in recent years as methods of separating multicomponent solutions. With this increase in popularity came an increase in the need to understand how multicomponent, concentrated solutions behave in a chromatography column. In the past, linear chromatography theory was sufficient to study the typically dilute solutions used for analytical purposes. For preparative and large-scale separations, where more concentrated solutions are involved, a multicomponent theory is needed.

In this paper a computer program based on one of these theories was used to simulate multicomponent ion-exchange chromatography. The theory, developed by Rhee, Amundson, Helfferich, and Klein (*1-6*), is

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used to examine displacement and elution ion-exchange cycles, demonstrating some of the behavior caused by interference. Conclusions about how displacer and eluent affinities affect separation speed and product concentration are then drawn.

In the theory, the following assumptions are made.

1. The fluid flows only in the axial direction at a constant interstitial velocity, v.
2. The packed bed has a constant void fraction, ε.
3. The effects of dispersion and diffusion are negligible.
4. The fluid and solid phases are locally in equilibrium.
5. The equilibrium follows a Langmuir-type isotherm,

$$q_i = \frac{q_{\max} K_i c_i}{1 + \sum_{j=1}^{j=n} K_j c_j} \tag{1}$$

where K_i and $q_{\max}$ are positive constants.

This theory was extended to ion-exchange systems where the values of K_i are very large. In this case, Eq. (1) can be approximated by

$$q_i = \frac{q_{\max} K_i c_i}{\sum_{j=1}^{j=n} K_j c_j} \tag{2}$$

This isotherm assumes that the relative affinities of all the components are constant, regardless of their concentrations. The relative affinity is defined as the ratio of sorbent affinity of species i to sorbent affinity of the most weakly bound species (K_i/K_{weakest}).

DISPLACEMENT CHROMATOGRAPHY

Consider a typical displacement chromatography cycle. First, a presaturant with a low affinity is displaced by a pulse of feed. After this pulse a high-affinity displacer is fed to the column, and finally, the column is regenerated with the weak-affinity presaturant (see Table 1 for conditions). The results for two cycles are shown in Figs. 1a and 1b. The presaturant exits the column first, followed by pure product bands at the concentration of the displacer (*4*). The displacer then exits, pushing the strongest affinity component from the column. Next, in the regeneration step, the presaturant pushes the displacer from the column, at which time the cycle begins over again.

TABLE 1
Conditions for Displacement Chromatography Simulations[a]

	Affinities			
	Displacer	Presaturant	Component 1	Component 2
Fig. 1a	10.0	1.0	1.1	1.4
Fig. 1b	1.41	1.0	1.1	1.4
Fig. 2a	1.28	1.01	1.0	1.273
Fig. 2b	1.28	1.10	1.0	1.273
Fig. 2c	1.28	1.27	1.0	1.273

[a]Displacer concentration, 1.0 *M;* presaturant concentration, 1.0 *M;* feed concentration of Component 1, 0.5 *M;* feed concentration of Component 2, 0.5 *M;* feed and eluent flow rates, 0.3 cm^3/s; feed pulse, 200 s; column length, 25 cm; column diameter, 2.5 cm; interstitial porosity, 0.4.

Although displacement chromatography is useful in that it produces pure product peaks, the choice of the displacer and presaturant affinities strongly affects the cycle time. From Figs. 1a and 1b it can be seen that the regeneration time controls the time between feed pulses. As the affinity of the displacer approaches that of the feed components, the regeneration time drops considerably. It can also be seen that the result of feeding the more strongly bound displacer to the column is to cause a shock wave to form which has pure displacer behind it. The speed at which this shock wave travels can be shown to be independent of the displacer affinity as long as it is the most strongly bound species (*2*). If the presaturant is the weakest-affinity species, all the components will travel at this shock-wave velocity. This implies that the separation time for a single feed pulse is not affected by the affinities of the displacer and presaturant if they are the strongest and weakest affinity species.

If the presaturant is the weakest affinity species (classical displacement chromatography), it should be close in affinity to the weakest affinity feed component. However, what happens if the affinity is greater than those of some of the feed components (this is no longer classical displacement chromatography)? Consider an equimolar feed whose components have affinities of 1 and 1.273, respectively. The displacer has an affinity of 1.28. Three cases where the presaturant has affinities of 1.01, 1.10, and 1.27 were examined. From Figs. 2a, 2b, and 2c it is obvious that the weakest affinity feed component quickly becomes more concentrated as the presaturant affinity approaches its affinity. Thus, the affinities of the presaturant and displacer should bracket those of the desired products as closely as possible.

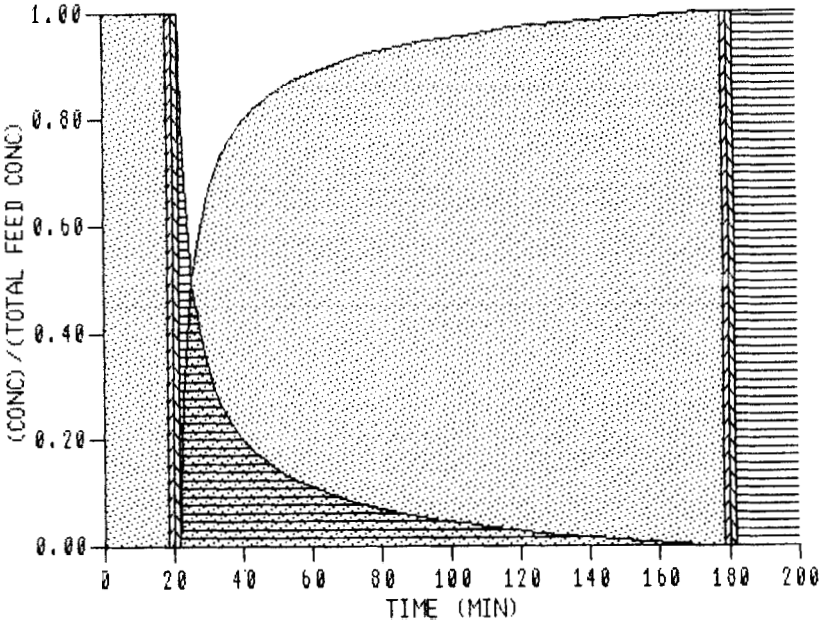

FIG. 1a. Effluent history of displacement chromatography. Strong-affinity displacer. Two cycles are shown. (▭) Displacer. (▭) Presaturant. (▨) Weak-affinity feed component. (▨) Strong-affinity feed component.

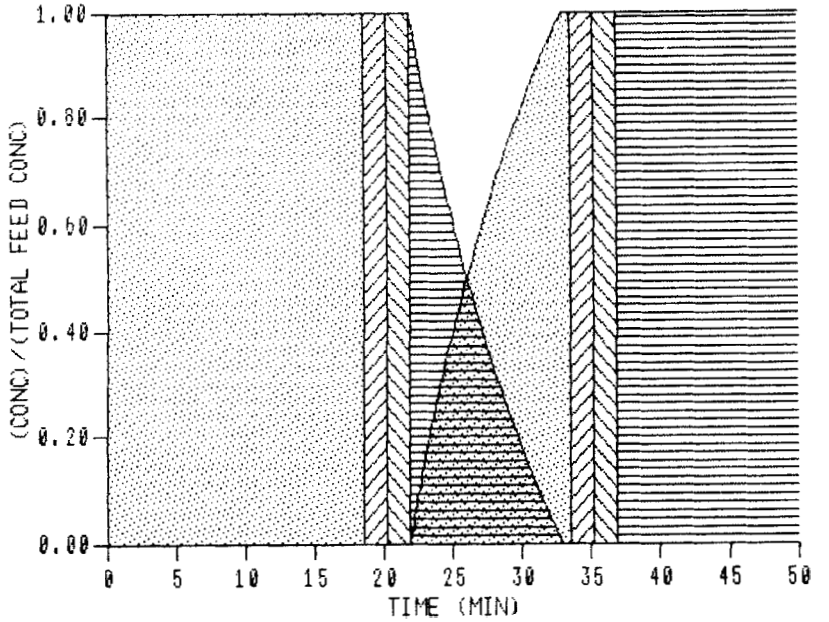

FIG. 1b. Effluent history of displacement chromatography. Weak-affinity displacer. Two cycles are shown. See Fig. 1a for key to area markings.

ELUTION CHROMATOGRAPHY

Next, the behavior of elution chromatography was examined. Now, the displacer and presaturant are the same. If the eluent affinity is varied, from Figs. 3a–g it can be seen that similar behavior occurs in all cases (see Table 2 for conditions.). In each case a feed component has a shock boundary and a diffuse boundary. The shock boundary exits before the diffuse boundary if the eluent affinity is less than the solute affinity, and after if the eluent affinity is greater than the solute affinity. Also, the width of the diffuse boundary decreases rapidly as the eluent affinity approaches that of the feed component. Although much of the behavior was similar in all the figures, some differences did occur.

Complete separation of the feed components occurs in Figs. 3b, 3c, 3d, 3e, and 3f. When the eluent displaces a slightly stronger species, as in Fig. 3b, a very steep diffuse wave occurs. This region is labeled A in Fig. 3b. In Figs. 3c and 3e, similar regions exist, but these regions are bounded by shock waves, labeled B. In Fig. 3f, like Fig. 3b, a steep diffuse wave occurs (labeled C) because the feed components are displacing a stronger affinity eluent. Thus the diffuse wave exits in the reverse sequence of that in Fig. 3b. In Figs. 3a and 3g, where the eluent has either very weak or very strong affinities, the feed components do not separate completely. For a weak eluent (Fig. 3a), the time between feed pulses is much longer than when the eluent has affinities between those of the feed components (Figs. 3c, 3d, and 3e).

Some rather complex behavior occurs in Fig. 3g and needs some explanation. Region A represents a small concentration plateau. This

TABLE 2
Conditions for Elution Chromatography Simulations[a]

	Affinities		
	Eluent	Component 1	Component 2
Fig. 3a	1.0	4.4	5.6
Fig. 3b	1.0	1.01	1.285
Fig. 3c	1.01	1.00	1.273
Fig. 3d	1.14	1.00	1.273
Fig. 3e	1.27	1.00	1.273
Fig. 3f	1.28	1.00	1.273
Fig. 3g	5.00	1.00	1.273

[a]Eluent concentration, 1.0 *M;* feed concentration of Component 1, 0.5 *M;* feed concentration of Component 2, 0.5 *M;* feed and eluent flow rates, 0.3 cm^3/s; feed pulse, 200 s; column length, 25 cm; column diameter, 2.5 cm; interstitial porosity, 0.4.

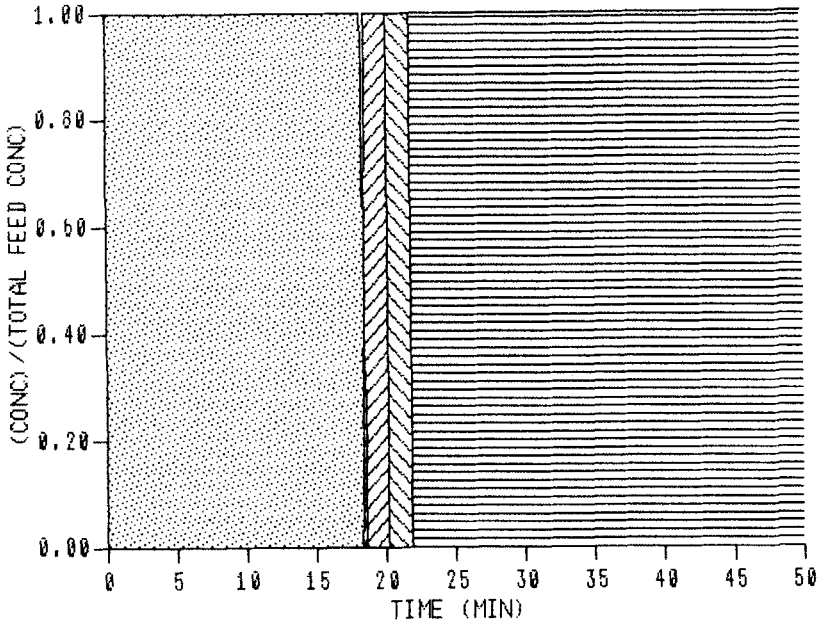

FIG. 2a. Effluent history of displacement chromatography using an intermediate-affinity presaturant. Presaturant affinity 1.01. See Fig. 1a for key to area markings.

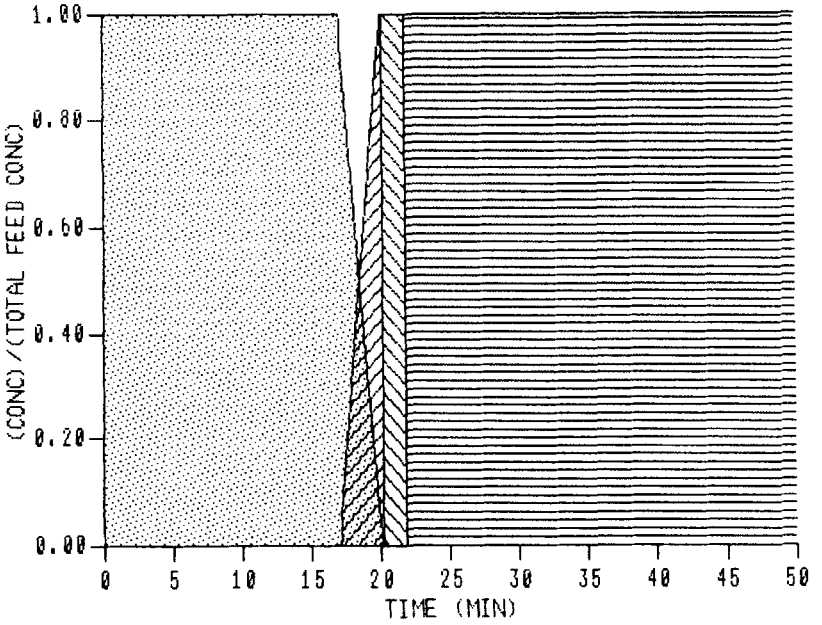

FIG. 2b. Effluent history of displacement chromatography using an intermediate-affinity presaturant. Presaturant affinity 1.10. See Fig. 1a for key to area markings.

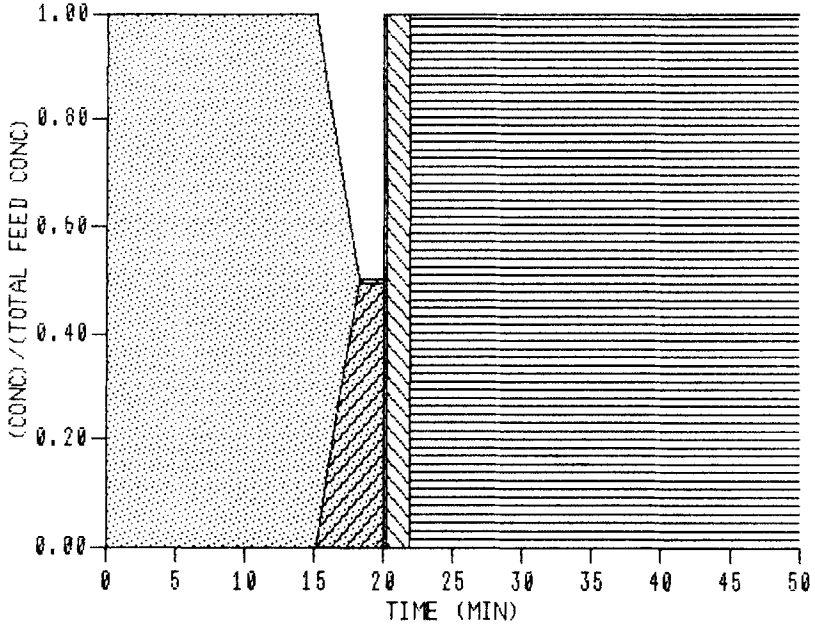

FIG. 2c. Effluent history of displacement chromatography using an intermediate-affinity presaturant. Presaturant affinity 1.27. See Fig. 1a for key to area markings.

plateau divides two diffuse waves. In the regions labeled B, diffuse waves occur because the weaker affinity feed components are displacing the stronger affinity eluent. The shock waves (labeled C) are caused by stronger affinity species displacing weaker ones. Shock wave D divides two regions of the same diffuse wave because interference between the various waves is still occurring. All the behavior described in this figure was confirmed using an independently written program (*7*) which employs the multicomponent chromatography theory developed by Helfferich and Klein (*2*).

It was found that the shortest cycles with complete separation occur when the affinity of the eluent is near to those of the stronger affinity feed components. Also, the shortest cycle (400 s) was much shorter than the shortest displacement cycle (670 s).

DISCUSSION

Both elution and displacement chromatographic behavior have been examined. The choice of which method to use depends upon the needs of

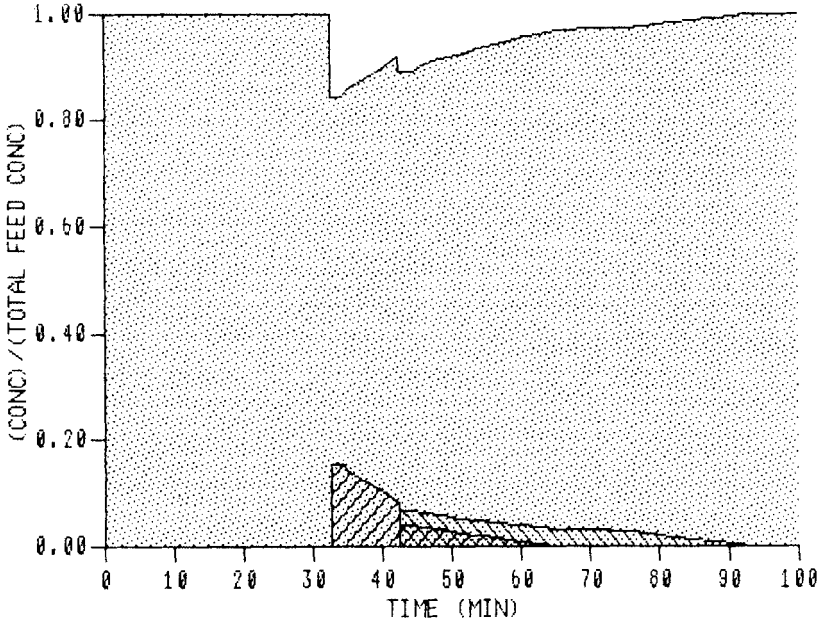

FIG. 3a. Effluent history for elution chromatography. Eluent has very weak affinity. (▨) Eluent. (▨) Weak-affinity feed component. (▨) Strong-affinity feed component.

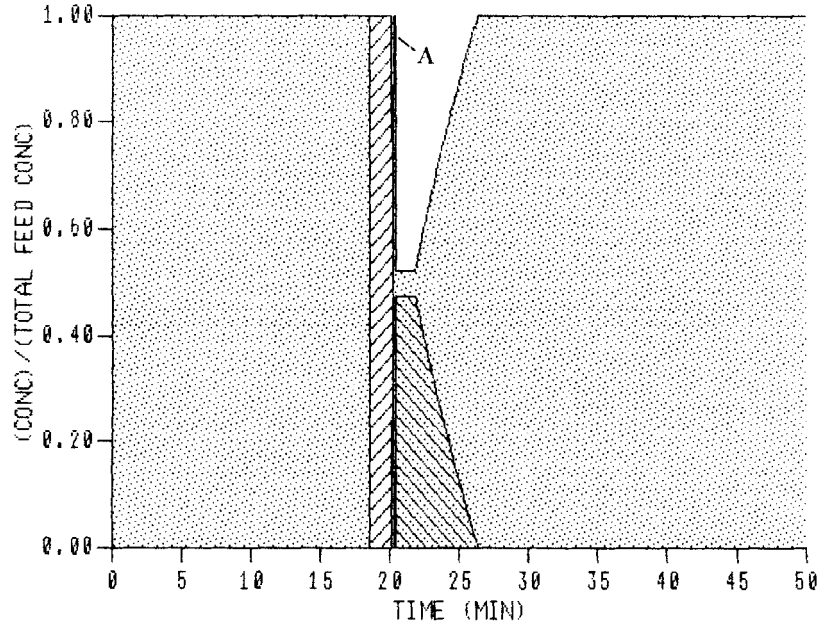

FIG. 3b. Effluent history for elution chromatography. Eluent has slightly weaker affinity than the feed. See Fig. 3a for key to area markings.

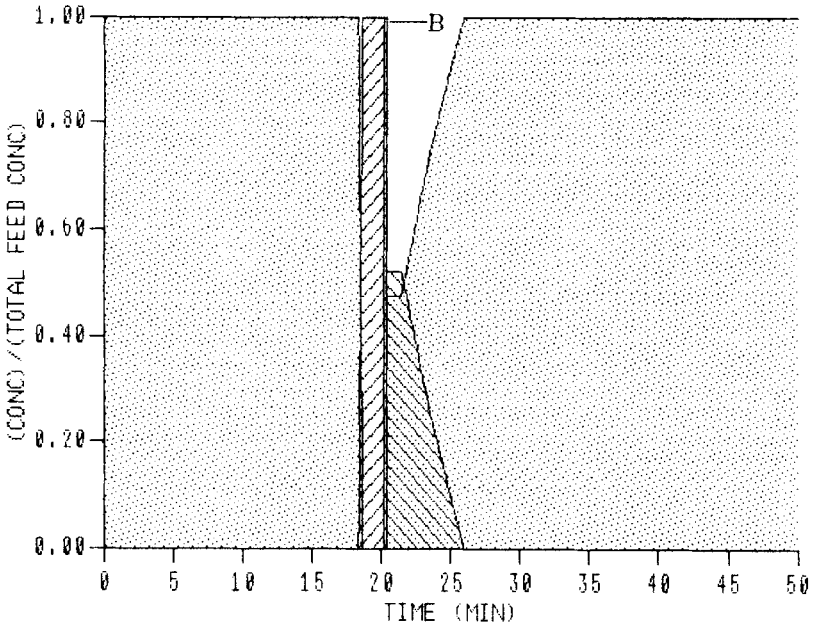

FIG. 3c. Effluent history for elution chromatography. Eluent has an affinity intermediate to feed components (1.01). See Fig. 3a for key to the area markings.

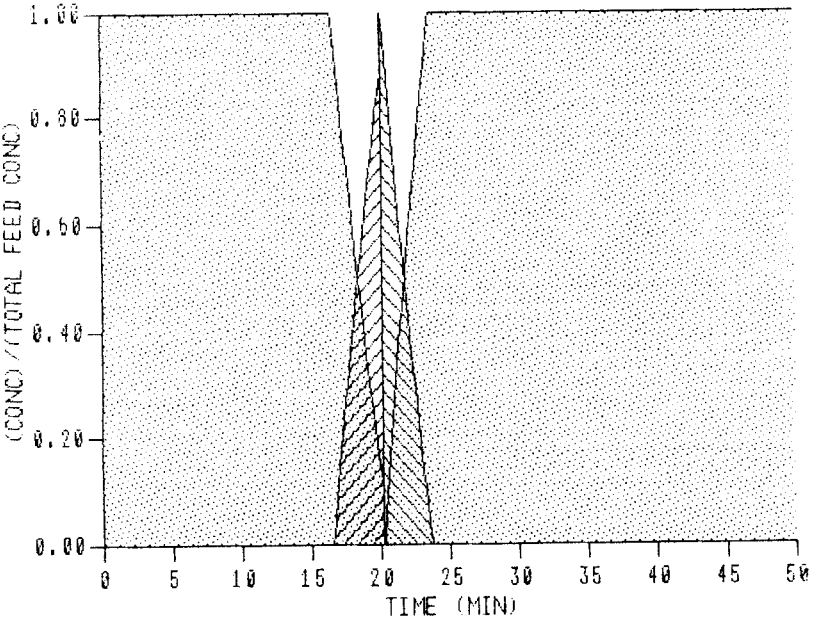

FIG. 3d. Effluent history for elution chromatography. Eluent has an affinity intermediate to feed components (1.14). See Fig. 3a for key to area markings.

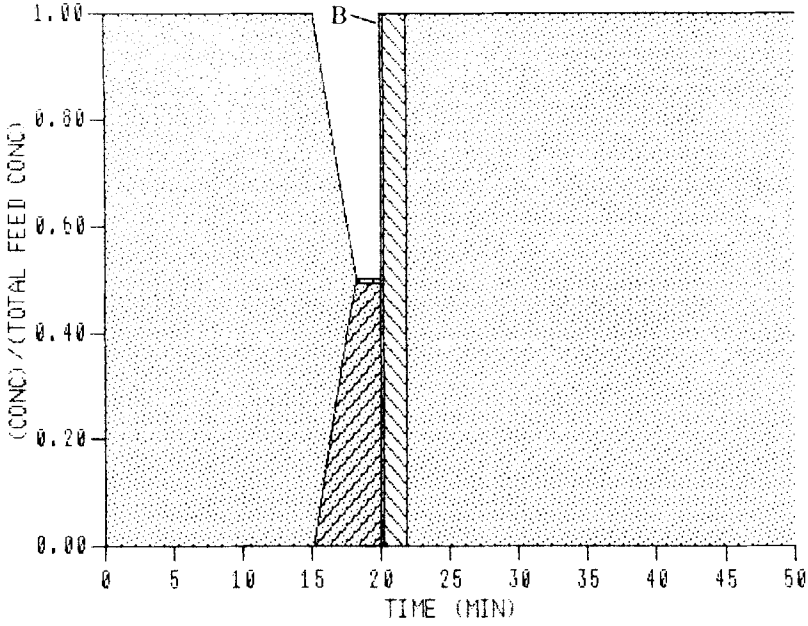

FIG. 3e. Effluent history for elution chromatography. Eluent has an affinity intermediate to feed components (1.27). See Fig. 3a for key to area markings.

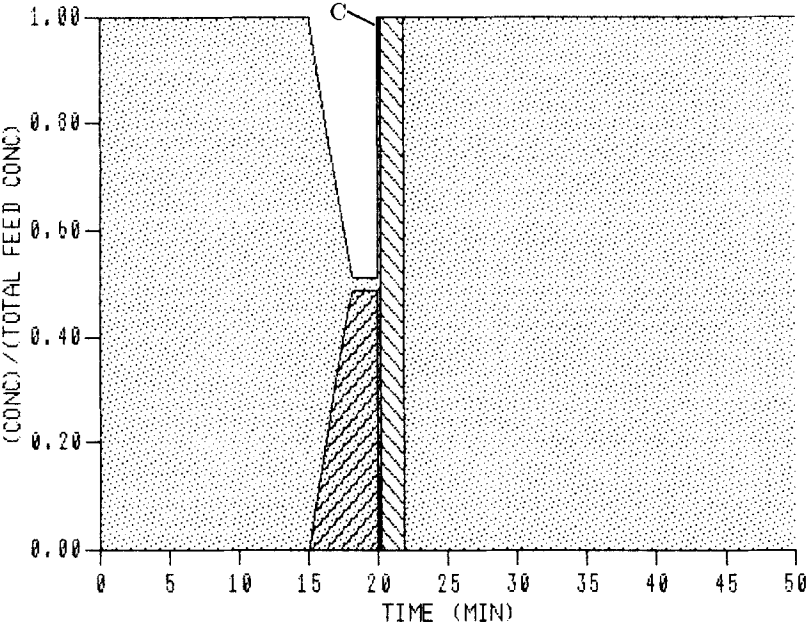

FIG. 3f. Effluent history for elution chromatography. Eluent has slightly stronger affinity than feed. See Fig. 3a for key to area markings.

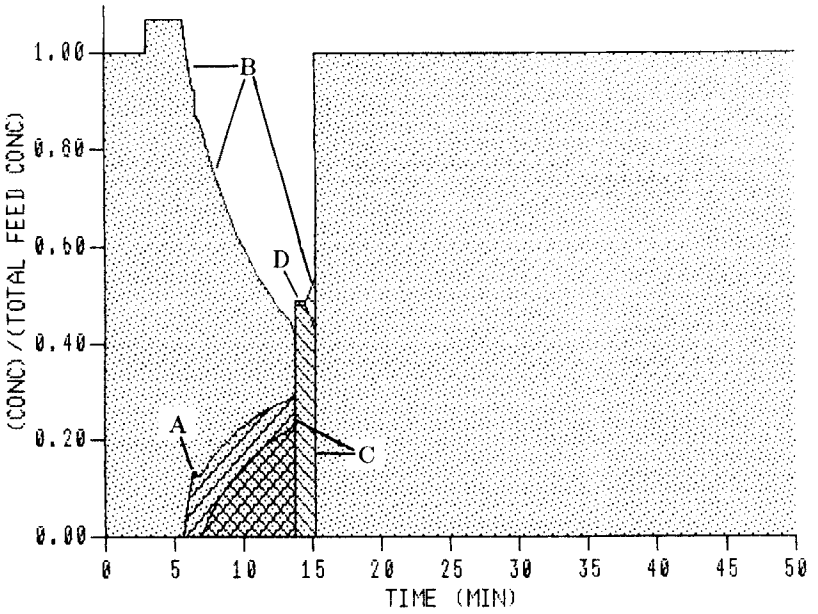

FIG. 3g. Effluent history for elution chromatography. Eluent has much stronger affinity than feed. See Fig. 3a for key to area markings.

the individual separation. For example, if pure products are needed, or the downstream separation costs are high, displacement chromatography should probably be used, with the desorbent and presaturant affinities closely bracketing those of the desired products. On the other hand, if purity demands are not as high, elution chromatography can produce shorter cycle times and thus higher throughput. The eluent should have an affinity that lies between or near those of the desired products, the position depending on the purity required. For short cycles the eluent should have an affinity near that of the highest affinity component in the feed.

The results in this paper are based on the equilibrium theory. In the equilibrium theory, diffuse waves are waves that continuously change over a range of times. Because of limitations of the computer solution, the diffuse waves are approximated by a large number of characteristic concentration step changes. In reality, this number of step changes should be infinite. Although the behavior is not representative of the actual system when only a few divisions are used, as the number of

divisions increases, the behavior rapidly approaches a limiting behavior. Between 10 and 30 divisions is usually sufficient to reach this behavior. More divisions are required for very diffuse waves (e.g., see Fig. 3a).

Another restriction on the results is caused by the inherent assumptions made in the equilibrium theory. In general, the results are less accurate when mass transfer resistances and axial dispersion are significant. The shock waves will exit as constant pattern waves. These waves will vary in zone width. When the mass transfer resistances are high or when axial dispersion becomes important, the patterns are much broader than when these effects are negligible. The diffuse waves are not as strongly affected by mass transfer or axial dispersion effects, and these parts of the effluent histories should be more accurate. In the extreme cases when kinetics control the system, the equilibrium theory is not very useful. This is likely to occur in systems with fast flow rates or when large molecules such as proteins are present.

For adsorption chromatography, results similar to those for ion exchange have been found. For elution chromatography it has been found that the eluent should have an affinity between those of the feed components (*8*). Also, commercial simulated moving bed systems typically use an eluent which has an affinity in-between those of the two feed components (*9*). In displacement chromatography it has been found that a critical displacer concentration is necessary to obtain the pure product bands observed in ion-exchange systems (*4*). Otherwise, beyond the critical concentration, displacement chromatography in adsorption systems is very similar to ion-exchange systems, and the conclusions drawn for ion-exchange systems are readily extended to adsorption systems (*10*).

SUMMARY

A multicomponent chromatography theory was used to analyze the effects of eluent affinity in elution chromatography and of displacer and presaturant affinities in displacement chromatography. It was found that the eluent should have an affinity between those of the feed components. In displacement chromatography the displacer and presaturant affinities should bracket those of the desired products as closely as possible. Also, displacement chromatography produces pure product peaks although the feed throughput is larger for elution chromatography. These conclusions are also valid for adsorption chromatography.

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