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COMMUNICATION

Partial Fractionation of Dyes by Cycling Zone Separation

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Cycling zone separation is a method of operating conventional separation devices that can be applied to a wide variety of separations such as adsorption, chromatography, and extraction. The basic technique developed by Pigford et al. (*1*) consists of cycling some thermodynamic variable in such a way that a continuously fed mixture is separated. The original work removed all solutes at once and has since been extended to multicomponent fractionation by Wankat (*2*). A tutorial review of cycling zone separation was recently presented by Wankat et al. (*3*) and includes theoretical analyses and a description of experimental results.

This note reports on the partial separation of two dyes in a countercurrent distribution (CCD) apparatus using sodium carbonate concentration as the cyclic variable. Initial results on concentration of phenol red by this technique were discussed by Wankat et al. (*3*). Further results on bromocresol green removal from water and the partial fractionation of bromocresol green from phenol red are presented here. These are the first reported experiments on fractionation by cycling zone separation. The separation technique presented here can easily be extended to more components, and has promise as a method for preparative separations.

TRAVELING WAVE CYCLING ZONE SEPARATION

Since the basic concepts of cycling zone separation for both single and multicomponent separation are discussed in detail elsewhere (*1–3*), only a very brief introduction will be given. In the system studied, the dye concentration of the feed is held constant but the concentration of sodium carbonate, the cyclic thermodynamic variable, is changed periodically.

The square wave used for single component separations is shown in Fig. 1(a) while Fig. 1(b) shows the staircase input used for multicomponent separations. For the chemical system used here the dyes tend to prefer the stationary 2-butanol phase at high Na_2CO_3 concentrations and the aqueous phase at low Na_2CO_3 concentrations. For removal of a single solute from water we would expect a periodic outlet concentration with large amounts of dye when the Na_2CO_3 concentration is low. For multicomponent separation the Na_2CO_3 concentration levels should be chosen so that at the intermediate level one dye moves faster than the Na_2CO_3

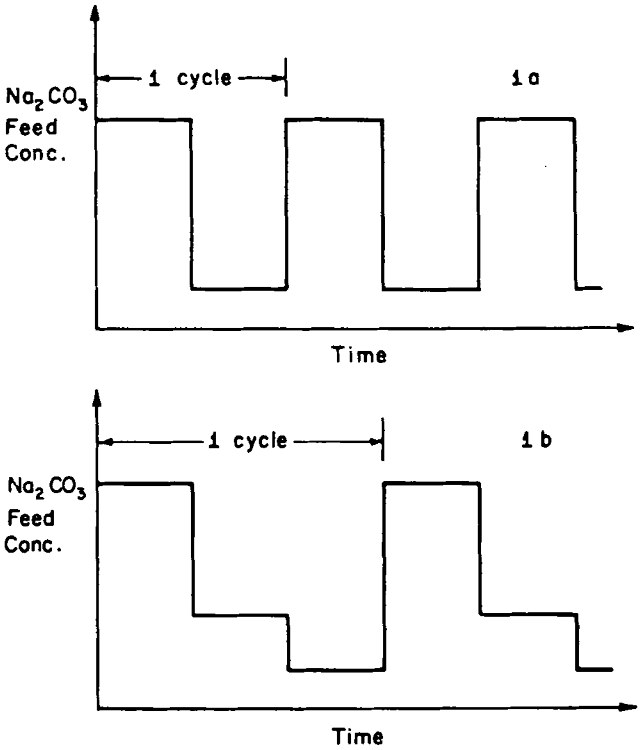

FIG. 1. Input concentrations of sodium carbonate. (a) Single dye removal. (b) Fractionation of two dyes.

and the other dye slower (*2*). Since this criterion could not be met for this system, only partial separations could be achieved.

EXPERIMENTAL

A CCD system consisting of five 15-ml centrifuge test tubes containing 5 ml of stationary 2-butanol phase and 5 ml of moving aqueous phase was used. The moving phase was transferred with a 10-ml glass syringe with a blunt needle. In all the experiments five transfer steps were used for each portion of the cycle shown in Fig. 1(a) or 1(b). For the removal of phenol red from water reported previously (*3*), Na_2CO_3 concentrations of 0.1 and 3.5 *N* were employed. Additional experiments with Na_2CO_3 concentrations of 0.1 and 5.0 *N* are discussed here. For bromocresol green removal, Na_2CO_3 concentrations of 0.0005 and 0.05 *N* were used. For the partial separation of phenol red from bromocresol green, Na_2CO_3 concentrations of 0.0005, 0.1, and 5.0 *N* were employed. The bromocresol green removal experiment was started with the test tubes initially containing no dye. The experiment with both dyes present was started with both phases containing a considerable amount of dye.

The dye concentrations were analyzed on a Bausch and Lomb spectrophotometer at 615 and 558 nm. At the dye concentrations employed, the absorbance of both dyes is linear with dye concentration. In addition, the absorbances of the two dyes are additive. From the linear calibration curves and the absorbance readings at the two wavelengths, the dye concentrations could be easily calculated.

Some emulsion problems were observed with this system. The problem was partially solved by allowing several hours (at least 4) for settling after each transfer step. In some cases extremely fine droplets of 2-butanol in the aqueous phase obscured the absorbance readings. Dilution of the sample with an equal volume of distilled water dissolved the 2-butanol and allowed an accurate reading. Even though the feed solutions were presaturated with 2-butanol, the volumes of each phase varied as the Na_2CO_3 concentration changed. This was particularly evident when the 5 *N* Na_2CO_3 was added to the CCD system.

RESULTS

The preliminary results for removal of phenol red from water were discussed by Wankat et al. (*3*). An additional experiment with phenol red showed that the separation could be increased by using a high Na_2CO_3

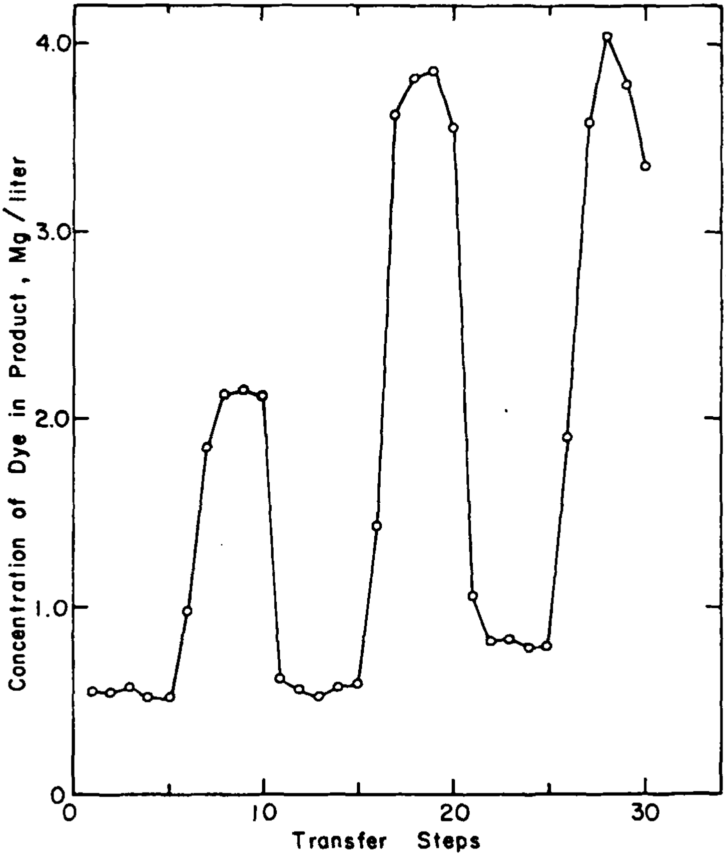

FIG. 2. Startup for cycling zone removal of bromocresol green from water. First half of each cycle exiting at 0.05 N Na_2CO_3. Second half of each cycle exiting at 0.0005 N Na_2CO_3.

concentration of 5 N instead of 3.5 N. The low concentration was 0.1 N in both experiments.

The results for removal of bromocresol green from water are similar and are shown in Fig. 2. It is noteworthy that much lower Na_2CO_3 concentrations are required to force the bromocresol green separation. Figure 2 shows the startup of the system and the approach to a repeating state. Note that the repeating state is rapidly approached since the second and third cycles are quite similar, but the outlet concentration is increasing.

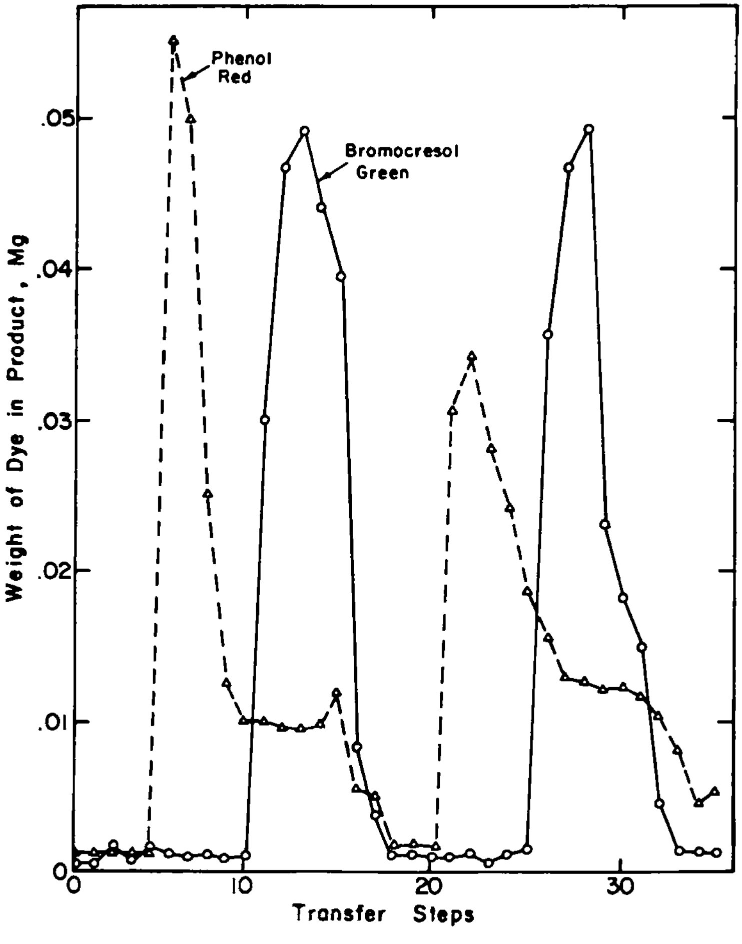

FIG. 3. Startup for cycling zone fractionation of phenol red from bromocresol green. First part of each cycle exiting at 5 *N* Na_2CO_3. Second part of each cycle exiting at 0.1 *N* Na_2CO_3. Third part of each cycle exiting at 0.0005 *N* Na_2CO_3. Feed concentration of each dye was 1 mg/ml.

Both dyes leave the CCD apparatus when the Na_2CO_3 concentration is low and are stored in the stationary phase when the Na_2CO_3 concentration is high. (Note that high and low are relative terms.)

The results for partial separation of phenol red from bromocresol green are shown in Fig. 3. At 5 *N* Na_2CO_3 concentration, both dyes are strongly attracted to the 2-butanol and very little material leaves the system. At 0.1 N Na_2CO_3 concentration the phenol red is not attracted to the stationary 2-butanol and exits from the column. The initial large peak occurs because the tubes in the CCD system initially had high phenol red concentrations. At 0.1 N Na_2CO_3 concentration, bromocresol green is still held up by the 2-butanol, but at 0.0005 N it is released to the aqueous phase and leaves the column. At 0.0005 N Na_2CO_3 concentration the phenol red stays in the mobile phase and passes through the system essentially without change at the feed concentration. This produces the large "shoulder" on the phenol red curve and prevents a complete separation of the two dyes. An additional experiment with both dyes showed similar results.

DISCUSSION

To achieve a clean fractionation of two or more solutes, the velocity of the thermodynamic variable through the system must lie between the solute velocities at the intermediate level of the thermodynamic variable (*2*, *3*). This would require that Na_2CO_3 move through the system at a slower rate than phenol red and faster than bromocresol green at a Na_2CO_3 concentration of 0.1 N. The first condition is not satisfied since the Na_2CO_3 essentially remains in the aqueous phase and it moves through the system at the mobile phase velocity [$A = 1.0$ in CCD theory (*2*, *3*)]. Since the velocity of the Na_2CO_3 wave cannot be readily controlled, only a partial separation is obtained. As shown in Fig. 3, the faster moving solute, phenol red, develops shoulders when the wave velocity of the thermodynamic variable cannot be controlled. This effect is also predicted by CCD theory (*2*, *3*) which illustrates that for good fractionation of solutes the wave velocity of the thermodynamic variable must be less than 1.0. If more dyes were present in the system, they could also be partially separated by adding more steps to the Na_2CO_3 wave shown in Fig. 1(b).

In Fig. 2 the bromocresol green concentrations in the product increase as the repeating state is approached. This occurs because the test tubes initially contained no dye, and the dye concentrations will build up to the repeating state values. Until the repeating state is reached, more dye will be input into the CCD system than leaves, and the mass balance over a complete cycle will not balance. In Fig. 3 the phenol red concentrations decrease as the repeating state is approached because of the initial high dye concentrations in each test tube for this experiment. The second cycle in Fig. 3 approaches the repeating state, but the phenol red mass balance is still high by over 10%. This is probably an indication that the repeating state has not yet been attained, but it may be due partially to experimental difficulties caused by emulsion formation and/or incorrect absorption readings. The low dye concentrations in Fig. 3 were too low to measure accurately. The second cycle shown in Fig. 3 is probably close enough to the repeating state to illustrate the basic pattern of the separation.

The cycling zone separation technique is also applicable to chromatography (*3*). Dore (*4*) has obtained partial separations of sugars using liquid chromatography, and additional research is being conducted in our laboratory.

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