Direct Visual Observation of Nonfoaming Adsorptive Bubble Fractionation

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In a recent publication, the authors' group reported on the partial separation of an ABS detergent solution in water at concentrations below the foaming threshold by the simple device of bubbling a gas through a column of the solution (*1*). This technique was called *bubble fractionation* (*2*), and some theoretical considerations for this novel operation have been recently offered (*4*).

Bubble fractionation is a member of a broad group of related techniques for which the name *adsubble methods* has just been proposed (*5*).

The present communication describes a method devised by the authors for directly observing and studying bubble fractionation in a very simple manner. In addition, some experimental results are presented and compared with theory.

EXPERIMENT

The method involves the use of a convenient dye as the solute to be concentrated. Several p.p.m. of commercial crystal violet chloride (91% hexamethylpararosaniline chloride) in distilled water has proved suitable.

A vertical glass column, several centimeters in diameter, is filled to a height of several feet with the dye solution. Nitrogen or air is then bubbled up through the column from a spinneret, porous disk, or other suitable sparger placed at the bottom. The surfaces of the rising bubbles adsorb the nonvolatile solute and carry it to the top of the column where it is released back to the liquid as the bubbles pass out. For best results many bubbles of small diameter are desirable. Also, care should be taken to avoid the introduction of impurities lest they preempt the surface and thus prevent the dye from concentrating sufficiently.

After several minutes of bubbling, a vertical gradient in color intensity should be observed, with darker (richer) solution at the top and lighter (leaner) solution at the bottom. With a similar but unbubbled column mounted alongside for purposes of comparison, it becomes visually evident that unlike gas desorption, bubble fractionation enriches the top while it strips the bottom. Gas desorption only strips.

Liquid samples can be readily withdrawn from the bubble column for easy analysis via colorimetric comparison. Alternately, the concentration can be measured in situ by means of a vertically traveling calibrated photocell mounted on the column.

While a narrow column is suitable for demonstration, the authors chose a wider one for study. It was 4.8 cm. wide and 122 cm. tall. Prehumidified nitrogen for bubbling entered through a coarse sintered glass dispersion tube located at the bottom of the column. Bubble sizes were neither controlled nor measured.

Samples were withdrawn from various levels of the column through rubber-capped side ports by means of a hypodermic syringe. They were then analyzed for dye concentration with a Beckman DB spectrophotometer in the visible range (5,830 A.).

RESULTS

In some tests the concentration attained at the top of the column was more than ten times that at the bottom. This represents a considerable degree of separation for so simple an operation.

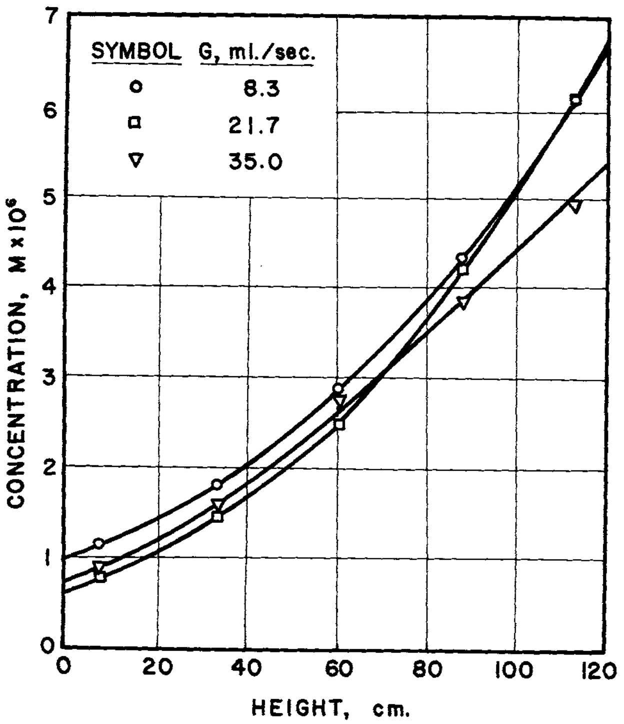

Fig. 1. Typical steady state concentration profiles for batchwise column operation at three different gas rates with an initial charge of 3.5 × 10^{-6} molar crystal violet chloride in water.

Figure 1 shows typical concentration profiles established at steady state in the column. These profiles, as well as others placed on file (*3*), show that the concentration increases up the column. This is in accord with the aforementioned theory (*4*). However the theoretical submodels based on a constant Γ can apparently be eliminated insofar as applicability to the present experimental system is concerned, since Equations (15) and (16) of said reference imply a linear profile, while the experimental profiles here are clearly not linear. The concentrations involved here are evidently too low for the bubble surfaces to saturate completely with adsorbed solute.

The self-consistency of the experimental data was checked by material balance by integrating each profile over the column to yield an average ordinate for each run, and then comparing each such ordinate with the corresponding charge concentration. These comparisons revealed a small loss of dye averaging about 15%, which may have been due to adsorption on the glass.

The increasing steepness of the slope for each profile agrees with the positive nature of the second derivatives from Equations (4), (8), (13), and (14). Of these four, Equations (13) and (14), which are derived from submodels partly based on equilibrium adsorption, are further supported by the rough semilogarithmic linearity of the profiles for most runs and the nonzero behavior of the slope at the bottom of the column for all but one run. These auxiliary plots have also been placed on file (*3*).

Figure 2 shows the effects of gas rate and charge (initial) concentration on the enriching ratio and on the

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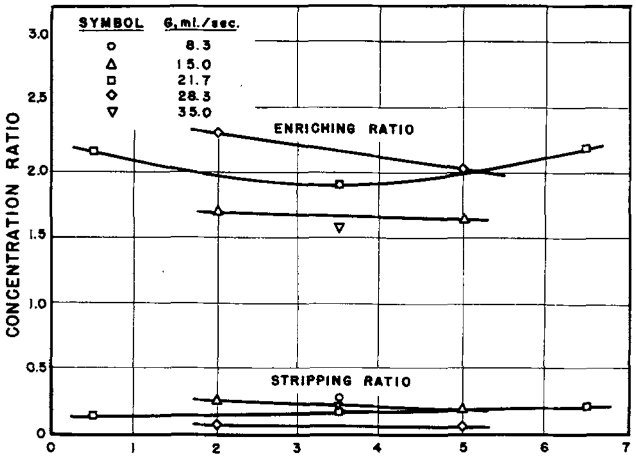

Fig. 2. Overall column performance.

stripping ratio. The latter ratio is defined as the concentration at the bottom of the column divided by the concentration in the charge. Correspondingly, the former is defined as the concentration at the top of the column divided by that in the charge. Dividing the enriching ratio by the stripping ratio yields the overall separation ratio.

Inspection of Figure 2 reveals that the curves are almost horizontally straight lines. This means that variation in the charge concentration was of comparatively little effect on the ratios, including the separation ratio. This agrees with Equations (4), (8), (13), and (14), but, as expected, not with Equations (15) or (16). Of course this comparison with theory is predicated on uniformity of bubble sizes from run to run. Such uniformity is an approximation at best.

Figure 2 also shows that, generally speaking, variation in the gas rate and hence in the bubble frequency resulted in only moderate changes in the ratios. This also supports the general theory, provided bubble sizes are again assumed uniform from run to run. Among the five gas rates employed, the prominent exception was 28.3 ml./sec., especially with respect to its stripping ratio. This however may have been just experimental error since the low concentrations at the bottom of the column are the most difficult to measure accurately.

CONCLUSIONS

Dilute aqueous solutions of crystal violet chloride provide a convenient and effective system for visualizing and studying bubble fractionation. Separation ratios of over 10 have been obtained in some cases, and the separation is clearly visible to the eye.

Experimental column performance is in approximate accord with recent theory. However, more data will be required to distinguish further among the several theoretical submodels. Tests with other dyes would be desirable too.

ACKNOWLEDGMENT

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NOTATION

G = gas rate, ml./sec.
M = concentration in solution, g.-mole/liter
Γ = concentration of adsorbed solute (surface excess), g./sq. cm.

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An Example of Unsteady Laminar Mixing in Power Law Fluids

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The solution given by Bird (*1*) for the unsteady velocity field produced in a pseudoplastic fluid by a suddenly accelerated moving wall appears to be the only nonsteady analysis for a power law fluid available in the literature. The present note treats the slightly more general problem of the decay of a velocity discontinuity between two parallel streams of fluid, which includes the problem considered in reference *1* as a limiting case. Solutions are obtained for both pseudoplastic and dilatant fluids. The analysis for the pseudoplastic case is nearly formally identical with that of reference *1*. The solution for the dilatant case contains a useful extension of Bird's analysis applicable to dilatant fluids.

We consider the time-dependent, parallel flow produced by momentum transfer between two adjacent laminar streams of fluid. To facilitate comparison with Bird's analysis, the notation of reference *1* will be used wherever appropriate. The initial velocities of the upper and lower streams are U_1 and U_2, respectively. For $t > 0$, the equation of motion for the fluid is (*1*)

$$\rho \frac{\partial u}{\partial t} = mn \left(\frac{\partial u}{\partial y} \right)^{n-1} \frac{\partial^2 u}{\partial y^2} \tag{1}$$

with boundary conditions

$$u = U_1 \qquad y = +\infty$$
$$u = U_2 \qquad y = -\infty$$

We look for a similarity solution of the form

$$u(y, t) = \tfrac{1}{2} (U_1 + U_2) + \tfrac{1}{2} (U_1 - U_2) f(\zeta)$$

where

$$\zeta = (n+1)^{-1} y \left(\frac{2^{n-1} \rho}{m\, t\, V^{n-1}} \right)^{1/(n+1)}$$