DEVELOPMENT OF A MULTISTAGED FOAM FRACTIONATION COLUMN

RC Darton, S Supino and KJ Sweeting

Department of Engineering Science
University of Oxford
Parks Road, Oxford OX1 3PJ, England

ABSTRACT

Surface active materials stabilise foam by adsorption at the gas/liquid interface. In foam fractionation, the foam is condensed to give a "foamate" liquid rich in surfactant. We have developed equipment and a process able to supply a number of stages of separation, working with an inert stripping gas. We have tested this with aqueous surfactant, and also with a surfactant which extracts and concentrates an organic solute. The measured liquid compositions are in good agreement with a model which describes the equilibrium using an adsorption isotherm, and which makes a mass balance for each stage in the column. The effect of liquid reflux is shown to be important. Possible applications of this process are in the fields of water purification, and the recovery of components such as proteins from solution.

PRINCIPLES

Mass balance

Foam fractionation is a method of separating the components of a liquid mixture based on the fact that the liquid near to an interface with a gaseous phase has a different composition to that of bulk liquid. If the surface layer is scooped up, it will be found to contain a higher concentration of some components and a lower concentration of others. Gibbs showed that the "surface excess" can be both positive and negative - surfactants have a large positive excess. In practice the surface layer is inevitably removed together with some underlying bulk liquid (termed entrainment by Lemlich [1]), and this reduces the change in concentration, as shown by the following simple mass balance for a perfectly mixed batch of liquid containing a surfactant, into which we bubble a gas (see Figure 1).

$$V_0 = V_1 + V_f \quad \text{and} \quad V_0 c_0 = V_1 c_1 + V_f c_1 + A\Gamma \quad \text{so} \quad c_0 - c_1 = \frac{A}{V_0}\Gamma$$

If we collapse the foamate to give a gas containing no adsorbed component and a liquid product, then the volumetric flow rate of foamate liquid is V_f and its composition after collapse is c_f, given by

$$V_f c_f = V_f c_1 + A\Gamma,$$

so $\quad c_f - c_1 = \dfrac{A\Gamma}{V_f}\quad$ and thus $\quad c_f - c_0 = A\Gamma\left(\dfrac{1}{V_f} - \dfrac{1}{V_0}\right)$

Foamate:
Liquid flow out V_f Concentration c_1
Area flow rate out A Surface excess Γ

Liquid flow in V_0
Concentration c_0

Liquid flow out V_1
Concentration c_1

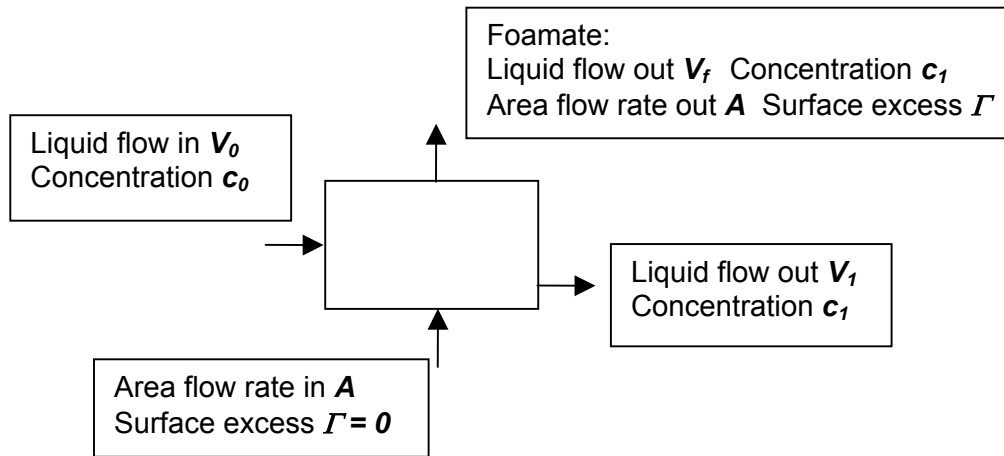Area flow rate in A
Surface excess $\Gamma = 0$

Figure 1 Flows around a well-mixed stage

Clearly in this simple example the enrichment occurring, given by $c_f - c_0$, is increased if the surface area provided by the bubble stream is high, if the amount of surface adsorption is high, and if the entrainment of liquid in the foamate is low.

Equilibrium
The surface excess of each component will be related to the composition of the liquid. In the simplest case, for a single component, we can consider that the surface is at equilibrium with the underlying bulk, and use the Langmuir adsorption isotherm, in which the saturated surface coverage is Γ_{sat}, and b is a constant. For an equilibrium stage then

$$\Gamma = \frac{c_1 \Gamma_{sat}}{b + c_1}$$

According to the Langmuir isotherm, the surface excess increases as the bulk concentration increases, though the rate of increase becomes very small as $c_1 >> b$. With most surfactants there is a concentration above which a second phase starts to form within the bulk, consisting of micelles. This critical micelle concentration (cmc) represents the limit of validity of the Langmuir isotherm, and above this concentration we can take the surface excess to be approximately equal to Γ_{sat}.

Foam Fractionation Equipment
The equipment used previously for foam fractionation has mostly supplied a single stage of separation. There has been little effort in developing equipment to give many stages of separation, and scale-up has been based on a simple enlargement of

laboratory devices, though there are some exceptions [2]. Multiple stages have been obtained by operating single columns in series [3]. A commonly used batch apparatus is that shown in Figure 2. The inverted J-tube holds a sample of liquid, and inert gas is bubbled through it. At the top, the foam overflows and dribbles into a collector where it coalesces and the gas escapes.
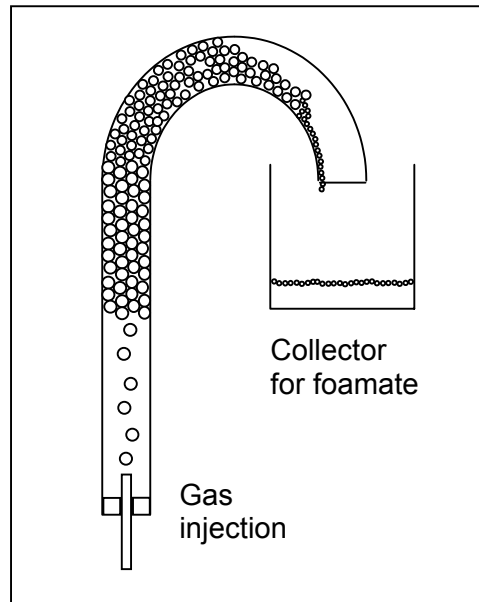

Figure 2 Laboratory apparatus for foam fractionation

It has been shown [1] that the height of the foam column can affect the degree of enrichment of the foamate, but to obtain more than one stage of separation, the residue must be discarded and replaced by foamate, and the experiment repeated. As with any batch fractionation, the concentrations change with time, and the first drops of foamate collected are richest in surface active material. As the experiment is continued, the enrichment of the foamate decreases.

THE CONTINUOUS FOAM FRACTIONATION COLUMN

A major problem with devising an apparatus suitable for continuous foam fractionation is that the foam must be reliably collapsed between stages, and the foamate liquid aerated to give a new foam, which in its turn must be collapsed again before the following stage. Most fractionation equipment designers are happy to avoid foam altogether, if they can, and so the continuous manufacture and destruction of foam poses a novel equipment design challenge.

We have developed an apparatus in which the foam on each stage is created by aeration with a sparger, and destroyed by a rotating paddle. As many stages as desired can be put into a vertical column, the paddles being mounted on a shaft that runs through the stages. Figure 3 shows the arrangement that we have used, with two stages of separation. For clarity in this diagram we have indicated the construction, which uses plastic and metal sheeting, and have not shown the foam or liquid levels.

For each stage there is a foam riser, aerated at the bottom with a sparger. At the top of the riser the foam flows up and over the weir onto the tray, where it encounters a sloping shelf with holes which direct flow into a cylinder. At the top of the cylinder is a rotating paddle which destroys the foam and throws the liquid towards the walls. Liquid drains down the upper surface of the sloping shelf and through a narrow slot between a lip at the bottom end of the shelf and the riser. A pool of liquid is present on each tray, held back by a weir formed by the top end of the riser, and this pool of liquid communicates freely with the bottom of the next riser, where there is another sparger generating foam to flow up to the next tray. On each stage the gas is vented from the space above the paddle. The column is rectangular in cross-section, being 160 mm wide and 80 mm deep. The risers are 80x40 mm in cross-section and the tray spacing is 140 mm.
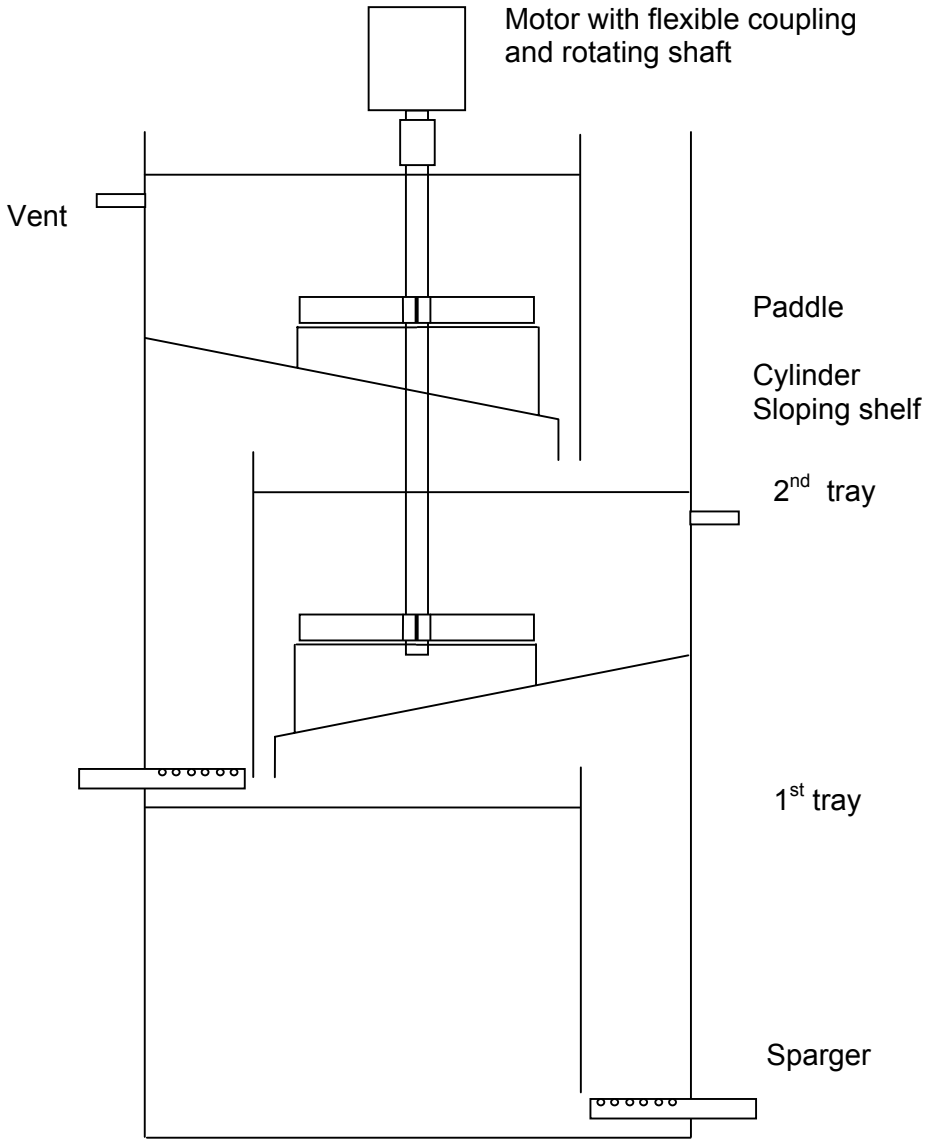

Figure 3 Multistaged foam fractionation column

EXPERIMENTS

With a multistaged device it is possible to introduce feed to an intermediate stage, and by using some foamate from the top stage as reflux liquid, to have both stripping and rectifying sections, in an analogous manner to conventional fractionation. However, in order to demonstrate the equipment, and check a mathematical model of the mass transfer, we have chosen to operate in batch mode. Liquid is charged to the bottom of the column (1 L), and also to the first and second tray (0.23 L each). Air flow to the spargers is begun, and the concentration of the liquid at the bottom (bulk) and on the trays is recorded as a function of time. Thus there is no withdrawal of material during the experiment, apart from the relatively small amounts taken as samples. We used the same flow rate to each sparger, varying between 0.3 and 1.0 L min^{-1}.

Triton experiments

In our first series of experiments, we used a non-ionic surfactant Triton X-100 (Octylphenoxypolyethoxyethanol), which is convenient for analysis with a spectrophotometer, having a well-defined absorbance peak at 277 nm. For this surfactant in water, Γ_{sat} is 3.677 10^{-6} mol m^{-2} and b is 2.112 10^{-3} mol m^{-3} [4]. The critical micelle concentration (cmc) is 0.3025 mol m^{-3}. Figures 4 and 5 show the concentrations on the top (2nd) tray and in the bottom compartment, for two values of the sparger gas flow rate. This surfactant system was used to develop the equipment and to check the model.
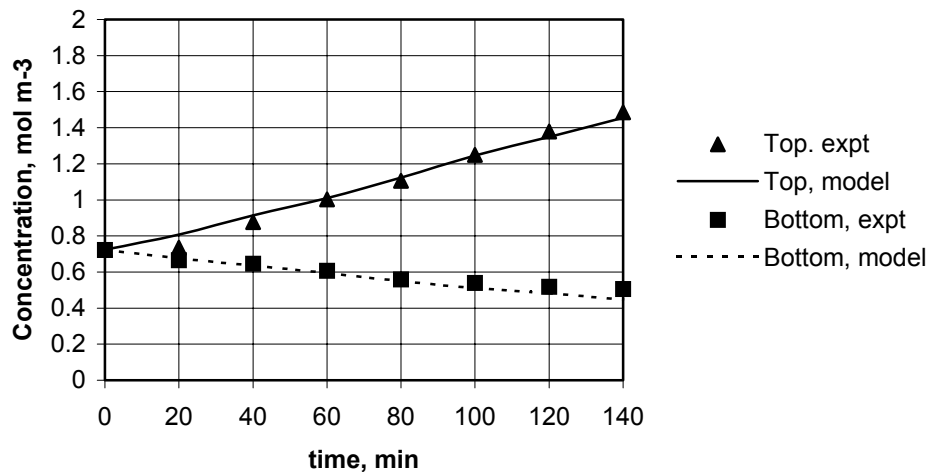

Figure 4 Concentrations of Triton X-100 at top and bottom
for sparger flow rates of 0.3 L min^{-1}

The inventory volumes and bubble size in the riser are recorded throughout each experiment, as they change slightly. The bubble diameters were generally between 4 and 9 mm, estimated by observation through the riser wall, using a calibrated template. As expected, the data show that higher rates of sparging cause the concentration difference between top and bottom of the column to develop more rapidly.
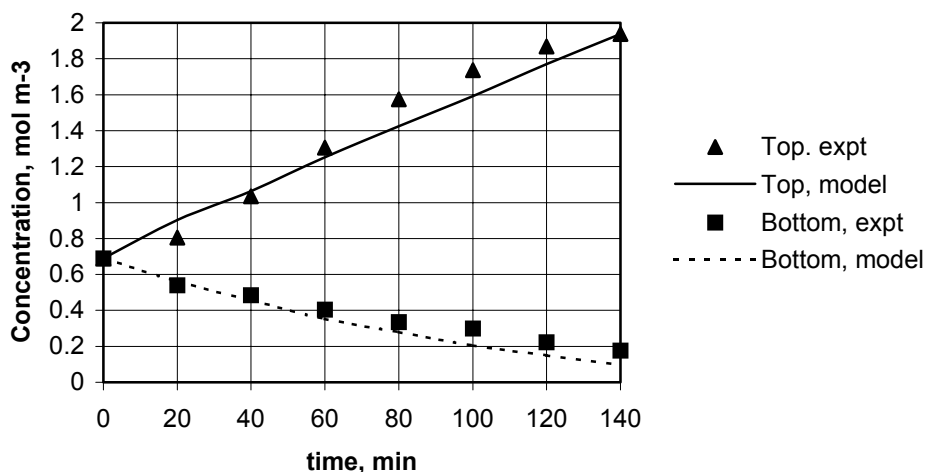
*Figure 5 Concentrations of Triton X-100 at top and bottom
for sparger flow rates of 1.0 L min^{-1}*

CPC Extraction Experiments

The second series of experiments was performed with cetyl pyridinium chloride (CPC), a cationic surfactant which stabilised the foam and which has a cmc value of 0.9 mol m^{-3}. Into the solution we introduced salicylic acid (added in the form of its sodium salt) which forms an ion pair with the basic CPC, and which is thus extracted in the foamate. Samples were again taken from the column during a batch experiment, and analysed by spectrophotometer. The CPC and salicylate could be distinguished in the analysis, since the former displays an absorbance peak at 258 nm, and the latter a peak at 297 nm.
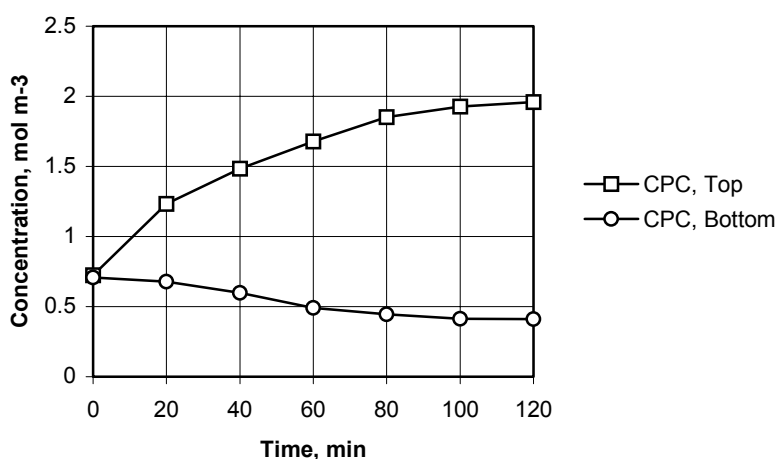

*Figure 6 First CPC batch. Concentrations of CPC at top and bottom
for sparger flow rates of 0.5 L min^{-1}*

Figure 6 shows the variation of CPC concentration in the first CPC batch experiment, and Figure 7 shows the simultaneous data for salicylic acid. The initial CPC concentration (0.7 mol m^{-3}) was chosen to be just less than the cmc value, and in this

experiment the salicylic acid was added in equal molar concentration to the CPC. At higher CPC concentrations the amount of foam can become rather excessive, particularly higher in the column where the concentration rises during the experiment.
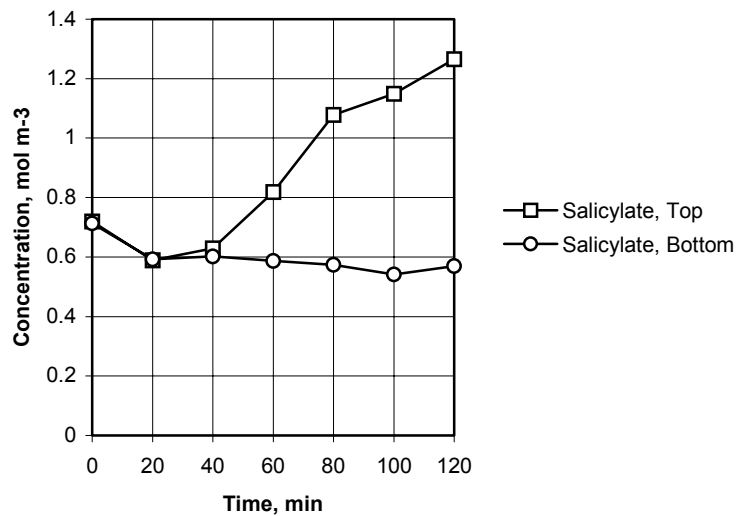

Figure 7 First CPC batch. Concentrations of salicylate at top and bottom for sparger flow rates of 0.5 L min^{-1}

In the second batch experiment with CPC/salicylate the initial concentration of salicylate was reduced by a factor 10, to be 0.07 mol m^{-3}. The variation of concentrations at top and bottom of the column are shown in Figures 8 and 9.
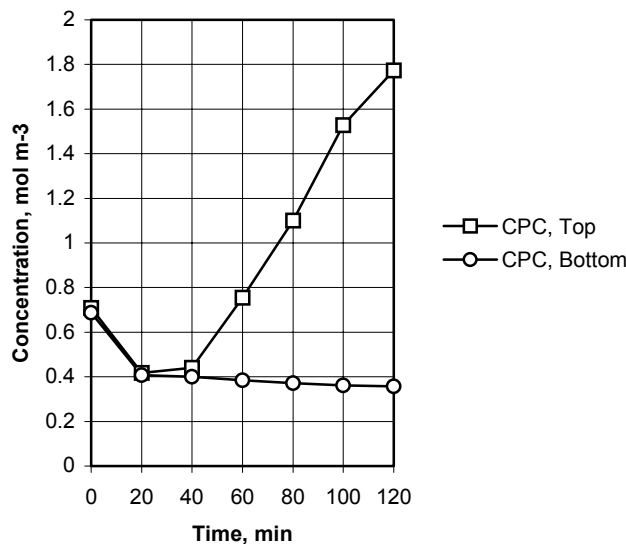

Figure 8 Second CPC batch. Concentrations of CPC at top and bottom for sparger flow rates of 0.4 L min^{-1}

This experiment demonstrated that a substantial increase in salicylate concentration could be achieved in the foamate, by means of CPC foam extraction. Figures 8 and 9 show that the concentration in the foamate was still increasing when the experiment

was stopped after 120 minutes. Salicylic acid is not itself surface active – this separation is solely due to the action of CPC in attaching the salicylate ion.
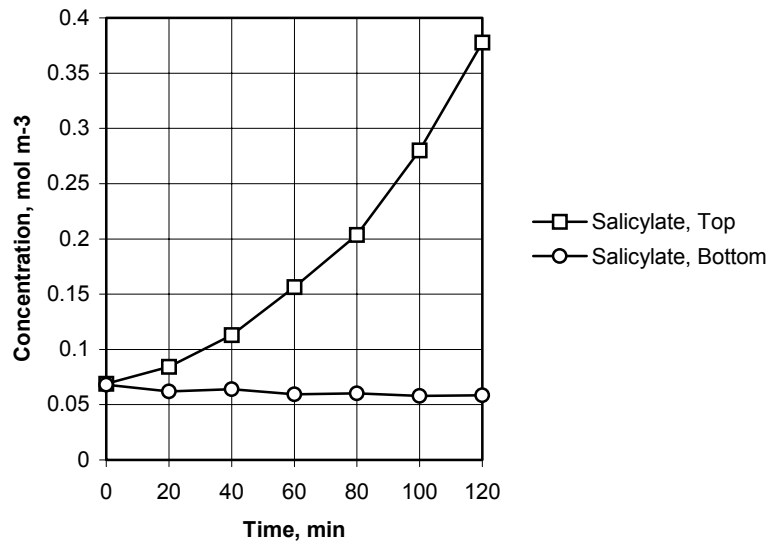

Figure 9 Second CPC batch. Concentrations of salicylate at top and bottom for sparger flow rates of 0.4 L min^{-1}

THE MODEL

Bubbles formed at the base of the riser adsorb surfactant onto their surface, and this is carried up in the riser, together with an entrained volume of bulk liquid. When the bubble is destroyed on the next stage up, the adsorbed surfactant is mixed into the liquid there, causing enrichment. Any entrained liquid is mixed in, and since the concentration increases from stage to stage up the column, this entrainment weakens the enrichment. A simple model of the foam fractionation process can be made by writing a mass balance for each stage, in which the key parameters are the interfacial area per unit volume of gas, and the volumetric flow rate of liquid entrained. Flows between stages are shown in Figure 10.

The flow rate of interfacial area, **A**, is calculated from the measured gas flow rate, and the measured bubble size in the riser, assuming spherical bubbles. We also need to know the liquid hold-up in the foam in order to calculate V_0, the flow rate of entrained liquid. The hold-up is estimated at around 10%, but the calculations turn out to be not very sensitive to the value taken so we took this constant value in all the simulations shown in Figures 4 and 5.

In this model we have to take account of liquid reflux. In our column, reflux arises because the liquid inventory of each stage is kept constant by the weirs on the trays. As entrained liquid arrives on the tray, an equal volume of liquid overflows the weir and falls into the rising foam. In Figure 10 the "Entrained liquid flow out" onto the upper stage is the liquid flow after the bubbles have escaped; this flow therefore includes the surfactant transported as adsorbed material on the bubble surfaces. We model the liquid flows as two streams that pass each other. A mass balance gives

$$c_1 + c_0 = c_{1B} + c_{0T}$$

and the fractionation occurring in the column depends on how the liquid streams are mixed.

No transfer in riser, $c_{1B} = c_1$

If there is no transfer between the entrained liquid flowing upwards and the reflux, then $c_{1B} = c_1$ and $c_{0T} = c_0$. The net upward transport of surfactant $V_0 (c_0 - c_{1B})$ is then equal to $V_0 (c_0 - c_1)$ and since at the initial condition the concentration on the upper stage is equal to that on the lower ($c_0 = c_1$), there is no net upward transport and no fractionation occurs: the bubbles merely serve to stir the liquid.
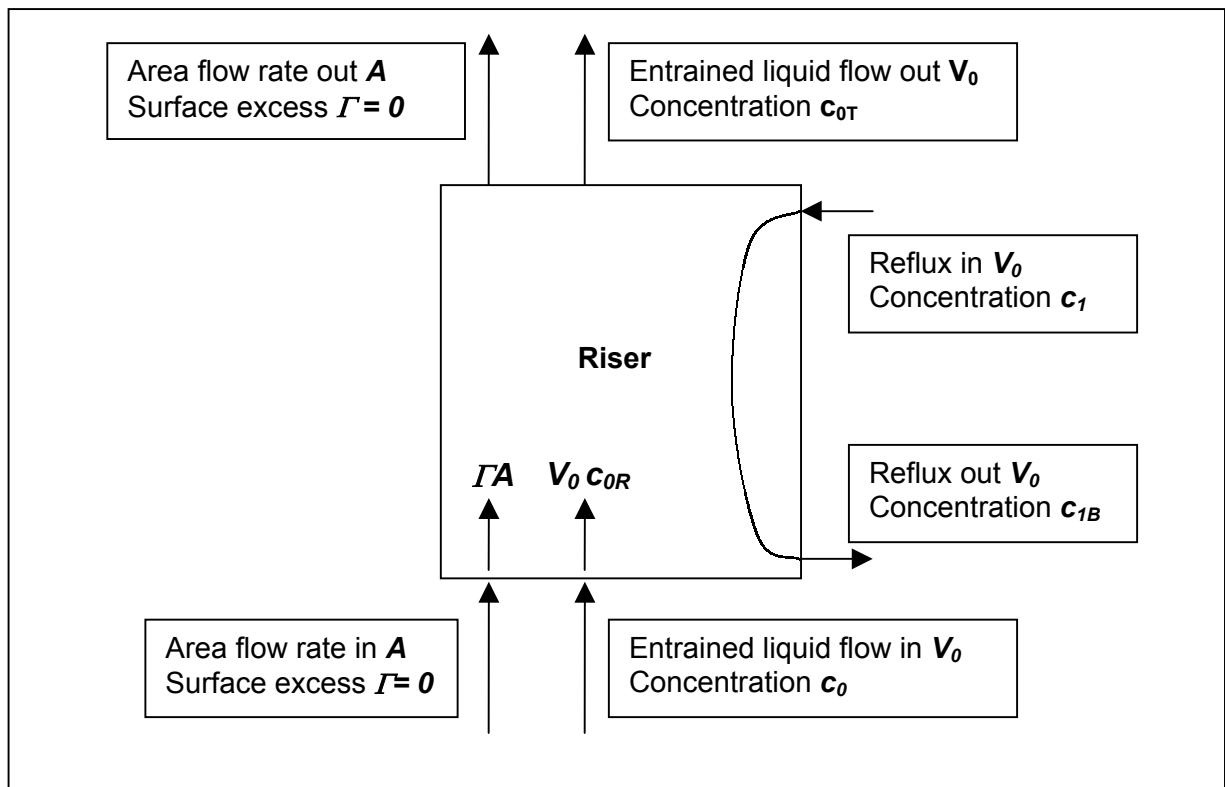

Figure 10. Mass balance around a riser, at total reflux

Maximum transfer in riser, $c_{1B} = c_{0R}$

However, the liquid entrained into the bottom of the riser is actually depleted, since

$$V_0 c_0 = V_0 c_{0R} + A\Gamma \qquad \text{so} \qquad c_0 - c_{0R} = \frac{A}{V_0}\Gamma$$

where c_{0R} is the concentration of the entrained stream inside the riser at its base. If we suppose that the refluxed liquid concentration falls to this value at the bottom of the riser, which is the lowest value possible, the net upward transport of surfactant is $V_0 (c_0 - c_{0R})$ which is equal to $A \Gamma$. A mass balance at the top end of the riser then shows that the entrained liquid concentration has reached c_1, its maximum possible

value, and after the adsorbed molecules have been mixed back into the entrained liquid, the liquid flowing into the upper stage has concentration

$$c_{0T} = c_1 + \frac{A}{V_0}\Gamma \ .$$

N stages of mixing in the riser

In practice it seems likely that the transfer between reflux and rising liquid will be somewhat less than the maximum possible. If the riser offers *N* mixing stages, the net upward transport of surfactant is

$$\frac{N}{N+1}A\Gamma - \frac{1}{N+1}V_0(c_1 - c_0) \ .$$

We have found our data for Triton to be well fitted with values of *N* between 4 and 10, and these have been used in computing the model results shown in Figures 4 and 5. Given the above expression for the transport in a riser, the rate of change of composition of liquid on a tray can be calculated. We have used an Euler predictor-corrector technique to solve the unsteady state balances.

We have solved the model for the case where all the entrainment is refluxed, so that the liquid flow rate *up* is equal to the liquid flow rate *down* (see Figure 10). It is straightforward to modify the balances for the riser should these flows not be equal. This would be the case if the feed entered on a continuous basis, and both foamate and a bottom product were continuously removed. Such processes are now being developed for protein fractionation [5], for example. If there are many stages of contact, and the net upward transport of surfactant is removed in a small volume of foamate fluid, then the concentration of this product (equivalent to the distillate in conventional fractionation) can be high.

CONCLUSIONS

An apparatus suitable for continuous multistaged foam fractionation has been developed and has proved suitable for separating surfactants from water. If appropriate surfactants are chosen, it is possible to use the equipment to effect a concentration of non-surface active solutes – this requires some affinity between the surfactant and the solute, and has been demonstrated using a cationic surfactant to extract an acidic solute. Comparison of the experimental data with a simple model based on mass balance and surface adsorption shows that mass transfer between foam and refluxed liquid is important to the separation.

ACKNOWLEDGEMENT

REFERENCES

1. Lemlich, R. (1972) *Adsorptive bubble separation techniques* Academic Press, New York

2. Rubin, E. and Gaden, E.L. (1962) *Foam Separation* in Schoen, H.M. (Ed) *New Chemical Engineering Separation Techniques* Wiley Interscience, New York

3. Morgan G., Wiesmann U., *Single and multistage foam fractionation of rinse water with alkyl ethoxylate surfactants* Separation Sci Tech 36 (10): 2247-2263 2001

4. Lu, H. Yang, Y., Maa, G. (1997) *On the induction criterion of the Marangoni convection at the gas/liquid interface* Ind Eng Chem Res 36 474-482

5. Du L.P., Loha V., Tanner R.D. (2000) *Modeling a protein foam fractionation process* Appl Biochem Biotech 84 (6), 1087-1099