A Theoretical Approach to Nonfoaming Adsorptive Bubble Fractionation

ROBERT LEMLICH
University of Cincinnati, Cincinnati, Ohio

A theoretical discussion is presented for the separation attainable via adsorption at the surfaces of bubbles rising up through a liquid solution. This heretofore neglected operation, which is called bubble fractionation, *differs from both foam fractionation and gas desorption.*

One important aspect of chemical engineering consists of understanding and improving the various techniques for separating materials. However, most of the effort so expended is devoted to the more usual methods of separation such as distillation and extraction. As a result, the obscure methods tend to remain obscure and their potential often lies dormant.

One such separation technique which has apparently been quite overlooked is that of bubble fractionation. [The name was recently proposed by the present author (*3, 7*).] It is basically a simple operation in which gas is bubbled up through a vertical column containing a surface-active liquid solution. Solute is adsorbed on the surfaces of the rising bubbles and carried upward to the top of the column where the bubbles break, releasing the solute back to the solution. This transport of solute establishes a vertical concentration gradient which can then be used as a basis for effecting a partial separation of constituents.

Bubble fractionation is an outgrowth of the author's work with foam fractionation (*1, 4, 8, 9*) but differs importantly from the latter operation in that no formation of foam is involved. Thus bubble fractionation can be applied to surface-active mixtures that, because of very low concentrations or some other reason, do not foam.

Bubble fractionation also differs from the familiar operation of desorption. The former involves adsorption on the bubble surface, while the latter involves diffusion of a volatile constituent into the bubble interior. By way of further comparison, it is of interest to note that bubble fractionation enriches the top of the column while it strips the bottom. Gas desorption only strips.

The operability of bubble fractionation has been demonstrated by the author in some preliminary batchwise experiments (*3*), using a vertical column containing a solution of technical monobutyl diphenyl sodium monosulphonate which was too dilute to foam. As shown in Figure 1*a*, prehumidified nitrogen from a single orifice was bubbled through the column for some hours to attain steady state. Samples of liquid were then withdrawn for analysis. The results for some runs showed the surfactant concentration at the top of the column to be as much as four times that at the bottom. This would seem to be promising indeed. The interested reader is referred to said publication (*3*) for further information.

In the present paper some theory is proposed for batchwise bubble fractionation. A subsequent paper will deal with future experimental results of a detailed nature in the light of this theory.

Extension to continuous flow operation with feed and takeoffs, as shown in Figure 1*b*, is more complicated. It will also be dealt with subsequently.

THEORY

Consider a batchwise bubble fractionation column, such as shown in Figure 1*a*, at steady state. As the bubbles rise they drag up relatively rich liquid at the rate L. This upflow L must be replaced by an equal downflow of relatively lean liquid. The resulting gross circulation, together with local circulation in the form of axial diffusion, limits the separation attainable.

A solute balance around the lower end of the column, such as represented by the envelope in Figure 2, gives

$$L\,y + a\,f\,\Gamma = L\,x + D\,A\,\frac{dx}{dh} \qquad (1)$$

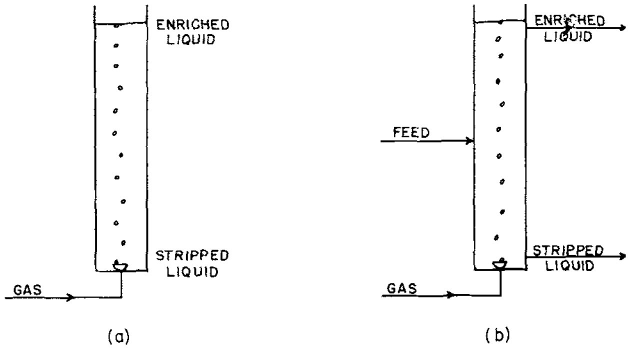
Preliminary studies indicate that the downward transport of solute by molecular diffusion is likely to be relatively small. Therefore D is primarily the eddy diffusivity.

The liquid being dragged upward is pictured as encapsulating each rising bubble with a quantity of liquid of indefinite outer shape but of outer surface a_o per bubble. The rate of solute diffusion across this outer surface may be expressed as $k_L a_o(x - y)$. Solute transfer across the inner surface a is of course adsorbed by the bubble surface. An instantaneous solute balance over the capsule gives Equation (2) (after dividing through by $dh/d\tau = v$).

$$\frac{L}{f}\,\frac{dy}{dh} + a\,\frac{d\Gamma}{dh} = \frac{k_L a_o}{v}\,(x - y) \qquad (2)$$

The familiar kinetic equation for reversible adsorption at low concentrations can be expressed by Equation (3) (again after dividing through by v).

$$\frac{d\Gamma}{dh} = \frac{k}{v}\left(y - \frac{\Gamma}{K}\right) \qquad (3)$$



(a) (b)

Fig. 1. Nonfoaming bubble fractionation. (*a*) Batchwise operation. (*b*) Continuous flow operation.

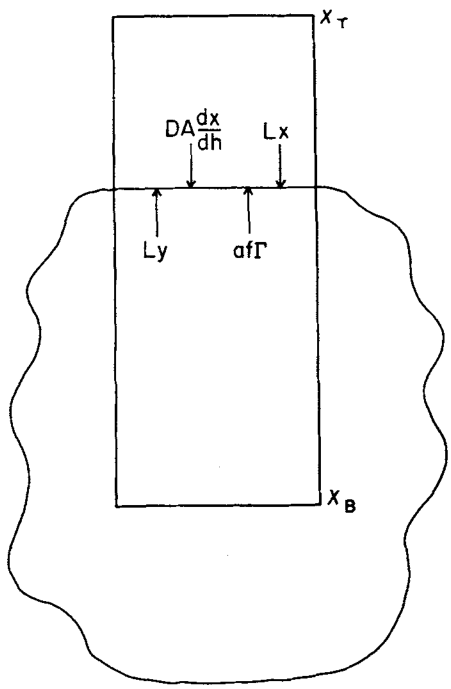


Fig. 2. Arbitrary hypothetical envelope for solute balance.

By allowing the significance of the constants in Equation (3) added scope, diffusional resistance at the bubble surface is incorporated. For higher concentrations, that is, where a large fraction of the bubble surface is covered with solute, or where the details of possible solute spill-off at the trailing edge of the bubble are of interest, Equation (3) can be replaced by the appropriate expressions (*2, 10*).

Equations (1), (2), and (3) can be solved simultaneously via the Laplace transform with the boundary conditions at $h = 0$ of $x = x_B$ and $\Gamma = 0$. Unfortunately, the final solution is very unwieldy. Accordingly, it is more instructive to consider certain limiting cases.

When axial diffusion (local circulation) is very small in comparison with gross circulation, the term $DA\ (dx/dh)$ may be dropped from Equation (1). The solution for this case is then

$$\frac{x}{x_B} = \frac{1}{2\sqrt{\beta^2+\alpha}}\left[(\beta + \sqrt{\beta^2+\alpha})\exp(\beta - \sqrt{\beta^2+\alpha})\gamma h - (\beta - \sqrt{\beta^2+\alpha})\exp(\beta + \sqrt{\beta^2+\alpha})\gamma h\right] \quad (4)$$

where

$$\alpha = \frac{4\,k_L\,a_o}{k\,a} \quad (5)$$

$$\beta = 1 + \frac{L}{K a f} \quad (6)$$

and

$$\gamma = -\frac{f k a}{2 L v} \quad (7)$$

For irreversible adsorption $\Gamma/K = 0$ so that Equation (4) [and later Equation (19)] may then be simplified by replacing β with unity.

On the other hand when axial diffusion is great compared to gross circulation, L may be equated to 0 in Equation (1), y equated to x in Equation (3), and Equation (2) simply dropped. The solution for this case is

$$\frac{x}{x_B} = \frac{B+N}{2B}\exp\frac{B-N}{2}h + \frac{B-N}{2B}\exp\frac{-B-N}{2}h \quad (8)$$

where

$$N = \frac{k}{v K} \quad (9)$$

$$M = \frac{k a f}{D A v} \quad (10)$$

and

$$B = \sqrt{N^2 + 4M} \quad (11)$$

For irreversible adsorption $N = 0$, in which event Equation (8) may be simplified to $x/x_B = \cosh \sqrt{M}\,h$.

For some systems the approach to equilibrium at the bubble surface may be so rapid that Equation (3) can be replaced by an expression for equilibrium, such as Equation (12) for low concentrations.

$$\Gamma = K y \quad (12)$$

At higher concentrations, Equation (12) should be replaced by the Langmuir isotherm or other appropriate equilibrium relationships (*2, 10*). A particularly interesting situation arises when the concentration is so high that the bubble surface is completely saturated everywhere in the column. This is considered later.

The solving of the simultaneous Equations (1), (2), and (12), together with the boundary condition of $x = x_B$ at $h = 0$, yields Equation (13) for the case where axial diffusion is negligible compared to gross circulation.

$$\frac{x}{x_B} = \exp\left[\frac{k_L\,a_o\,K\,a\,f^2\,h}{(L + K a f) v L}\right] \quad (13)$$

For the reverse situation, that is, when axial diffusion is great compared to gross circulation, the simplifications referred to earlier apply: $L = 0$, $y = x$, and Equation (2) is dropped. Then, instead of Equation (13), the result is

$$\frac{x}{x_B} = \exp\left[\frac{K a f h}{D A}\right] \quad (14)$$

If, as mentioned earlier, the bubble surface in some system were to completely saturate with solute at once (so that Γ is constant), separation in the column would still be achievable. The result with negligible axial diffusion would be

$$x - x_B = \frac{k_L\,a_o\,a\,\Gamma\,f^2\,h}{v\,L^2} \quad (15)$$

With negligible gross circulation instead, it would be

$$x - x_B = \frac{a\,\Gamma\,f\,h}{D A} \quad (16)$$

In each of the above solutions, namely, Equations (4), (8), and (13) through (16), setting $h = H$ gives either x_T/x_B which is the overall separation ratio, or $x_T - x_B$ which is the overall separation difference. However, to find any x independent of x_B requires a solute balance against the initial charge. Such a balance involves the solute which is adsorbed on the rising bubbles, as well as that in the upflowing and downflowing liquids. It may be written as

$$\frac{K a f}{v}\int_o^H y\,dh + \frac{L}{v}\int_o^H y\,dh + \frac{L}{v'}\int_o^H x\,dh = C_i H A \rho_i \quad (17)$$

However, the adsorbed holdup is likely to be small. Also, in a column of sufficient diameter, $v' << v$. Under these circumstances the first two terms in Equation (17) may be neglected so that the equation reduces to

$$\int_o^H x\,dh = C_i H \quad (18)$$

By combining Equation (18) with say Equation (4), one obtains

$$\frac{x}{C_i}=\frac{H\alpha\gamma[(\beta+\sqrt{\beta^2+\alpha})\exp(\beta-\sqrt{\beta^2+\alpha})\gamma h-(\beta-\sqrt{\beta^2+\alpha})\exp(\beta+\sqrt{\beta^2+\alpha})\gamma h]}{(\beta+\sqrt{\beta^2+\alpha})^2[1-\exp(\beta-\sqrt{\beta^2+\alpha})\gamma H]-(\beta-\sqrt{\beta^2+\alpha})^2[1-\exp(\beta+\sqrt{\beta^2+\alpha})\gamma H]} \tag{19}$$

Corresponding relationships can be obtained by combining Equation (18) with Equation (8), (13), (14), (15), or (16).

DISCUSSION

Equations (4), (8), and (13) through (16) all show that the degree of separation increases with column height. This is apparently confirmed by the results of the preliminary experiments (*3*) mentioned earlier. However, with respect to Equations (4) and (13), it should be noted that the separation ratio measured experimentally was based on liquid samples which do not distinguish between upflow and downflow. Thus any comparison with those preliminary data is necessarily approximate.

The theoretical results for gross circulation also indicate that variation in bubble frequency should be without effect. Changing the frequency should simply change the rate of surface generation and the rate of liquid upflow in proportion. This, too, is apparently in agreement with those preliminary experiments, since raising the frequency from 120 to 250 bubbles/min. was without appreciable effect on the separation. Of course, to the extent that D is proportional to f, the results for axial diffusion are also in apparent agreement.

The experimental results showed a marked decrease in separation ratio when the column diameter was increased. Since only a single stream of bubbles was employed, the observed reduction in separation could be due to a diminished wall effect which makes for an undesirable increase in L, and/or it could be due simply to the increase in A which promotes axial diffusion. Both explanations are in accord with the theory presented.

For the particular system employed in those experiments, surface tension measurements (*1*) combined with Gibbs' equation for adsorption (*5, 6*) reveal that only a small fraction of the bubble surface was covered with solute at the concentrations involved. Thus use of the linear isotherm, which is implicit in most of the theoretical development in the present paper, is also applicable to that experimental system.

Unfortunately, the experimental results were too scant and preliminary to support any firm quantitative comparison with the theory. Such comparison must await a subsequent paper by which time more extensive and refined data should be available.

SUMMARY

A theory for batchwise column operation was developed for the novel separation process of bubble fractionation. The theory involves the adsorption of solute at the rising bubble surfaces, the upflow of depleted liquid which is dragged along, the balancing downflow, and axial back-diffusion.

Results of the theoretical analysis imply that the degree of separation increases with column height, decreases with column diameter, but is independent of bubble frequency. This is in accord with preliminary experiments in columns with a single gas orifice. More detailed comparisons must await further experimentation.

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NOTATION

a = surface area of a bubble, sq. cm.
a_o = surface area of the dragged liquid encapsulating a bubble, sq. cm.
A = effective cross-sectional area of the column, sq. cm.
B = modulus, cm.$^{-1}$
C_i = initial solute concentration in the charge, mass fraction
D = axial eddy diffusivity, g./(cm.)(sec.)
f = bubble frequency, sec.$^{-1}$
h = height of any point in the column, cm.
H = total height of the column, cm.
k = kinetic coefficient, g./(sec.)(sq. cm.)
k_L = mass transfer coefficient, g./(sec.)(sq. cm.)
K = equilibrium constant, g./sq. cm.
L = rate of liquid upflow and downflow within the column, g./sec.
M = modulus, cm.$^{-2}$
N = modulus, cm.$^{-1}$
v = upward velocity of a bubble, cm./sec.
v' = downward velocity of the liquid downflow, cm./sec.
x = solute concentration in the liquid downflow (or in the bulk in the absence of downflow), mass fraction
y = solute concentration in the liquid upflow, mass fraction

Greek Letters

α = dimensionless modulus
β = dimensionless modulus
γ = modulus, cm.$^{-1}$
Γ = concentration of adsorbed solute, g./sq. cm.
ρ_i = initial density, g./cc.
τ = time, sec.

Subscripts

B = bottom of column
T = top of column

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