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General Survey of Adsorptive Bubble Separation Processes*

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Summary

In this article we present a general survey of adsorptive bubble separation processes. These separation methods involve the use of selective adsorption at gas–liquid interfaces, the interfaces being generated by gas bubbles in aqueous media. A variety of processes based on this mechanism have been developed, and these methods are described in this review. The underlying concepts in this field are then explored so that the similarities between the methods can be seen. Engineering applications, as well as our own work on analytical applications, are presented. Suggestions are also made as to future potentialities for these adsorptive bubble separation processes. Finally, to place these methods in proper perspective, the techniques are compared to such widely used processes as ion exchange and liquid-liquid extraction.

INTRODUCTION

Renewed interest has occurred in the last few years in the use of foam separation and related processes for separation and purification problems. Most workers are familiar with the relatively old process of ore flotation or mineral dressing in which separation is the result of density differences in macro particulates (*1*). However, it is also possible to use foams for the separation or removal of micro particulates of a colloidal nature and indeed of species on the

* Presented September 25, 1968, at the Tripartite meeting of Chemical Engineers, Montreal, Canada; Symposium—"Unusual Methods of Separation."

molecular or ionic level. As we shall see, it is even possible to effect separation without the use of a foam itself, i.e., with only the passage of gas bubbles through the bulk medium.

The common theme in all these methods is the use of adsorption on gas bubbles produced in bulk liquid media—thus the suggested generic name of adsorptive bubble separation processes. The techniques in part differ in the method in which the enriched gas–liquid interfaces are removed from the bulk media. In certain cases foam columns are used, whereas in other cases the material adsorbed on the bubbles is deposited in a second liquid phase, which is immiscible with the first one.

At the outset it may be stated that these processes are effective as economic large-scale removal methods for materials at relatively low concentration. Thus many of the applications have been in the chemical engineering field. For example, foam separation has been examined for use in the waste water field (2), the nuclear waste removal field (3), and the microflotation of bacteria and algae (4). We hope to show in this article that there are areas other than those above that have a great deal of potential for the foam field. This is especially true in the separation and purification of biological systems.

The purpose of this review is to familiarize the reader with the current state of the art of adsorptive bubble separation processes. We shall first indicate the scope of the field by an examination of the various processes presently being developed or in use. The principles common to the methods will then be explored. In the latter area, it is not our aim to be highly theoretical, for drainage in a foam column is an exceedingly complicated phenomenon, but rather we hope to indicate some of the underlying concepts of this field. We shall then describe some of the engineering applications of these techniques as well as our own work on the analytical applications. Suggestions will also be made as to where foam methods could be effectively used. Finally, to place these processes in proper perspective, we shall compare the techniques to such widely used separation processes as ion exchange and liquid–liquid extraction.

DEFINITIONS

An interest picked up in the adsorptive bubble separation field, workers of various disciplines became involved in the developmental research. Confusion arose in the literature as to the naming

of these methods, and it was not uncommon to find several authors using different names for the same techniques. As a result of a Gordon Research Conference session on foam separations, five of the people in the field recommended a set of nomenclature that was published in 1967 (*5*).

Figure 1 represents a diagram of the total nomenclature scheme. An obvious division of adsorptive bubble separation methods is in terms of the collection procedure for the enriched gas–liquid interfaces. If a foam is involved in the process, then the term foam separation is applied, whereas nonfoaming adsorptive bubble separation involves no production of foam.

Foam separation must be further subdivided in terms of the nature of the species being separated. If species being removed are part of a homogeneous solution, then the term foam fractionation would be applied. This would be the case, for example, in the removal of surface-active agents such as salts of fatty acids and alkylbenzene sulfonates (ABS) (*6*).

If the species being separated from the bulk liquid media are insoluble particulates, then the term flotation or froth flotation is applied. Flotation can naturally be subdivided into seven parts, as listed in Fig. 1. Ore flotation and macroflotation represent the removal of macroscopic particles by foaming. Actually, both processes are the same, but it was felt necessary to take special note of the mineral dressing process, and thus ore flotation denotes the flotation process for the separation of minerals (*1*). Microflotation, quite obviously, represents the removal of microscopic particles by foaming. This process especially deals with the flotation of microorganisms (*7*) and colloids (*8*) (i.e., colloid flotation). A great deal of untapped potential exists for microflotation, and we shall have something to say about this later. As the name implies, adsorbing colloid flotation involves the flotation of colloidal particulate upon which dissolved material is adsorbed. In this case the major objective is the removal of the dissolved material rather than the colloidal particles. Again, we shall explore this method in this review article.

Precipitate flotation, first developed by Baarson and Ray in 1963 (*9*), involves the flotation of precipitates, the precipitating agent not being the surfactant. For those precipitates which are difficult to handle because of their gelatinous character, this method holds promise as a means for the removal of precipitate from the bulk liquid media. Finally, in the flotation area we have ion flotation and

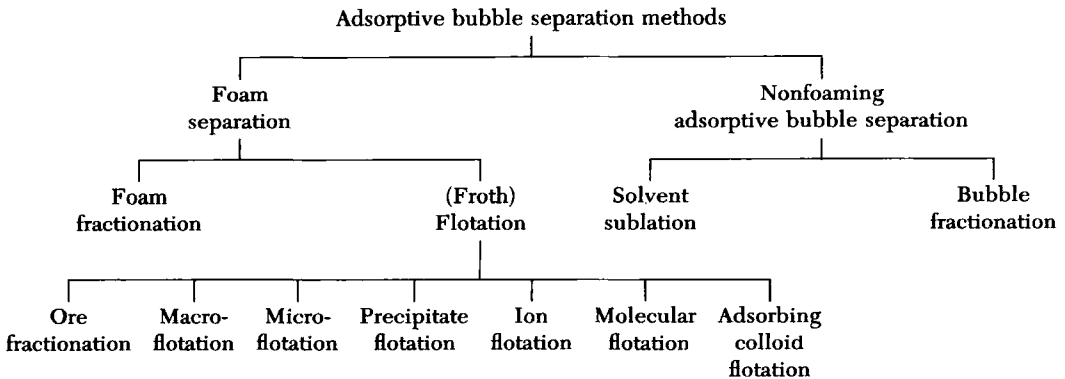

FIG. 1. Schematic representation of subdivisions of adsorptive bubble separation processes. [From *Separation Sci.*, **2**, 401 (1967), by permission of Marcel Dekker, Inc.]

molecular flotation. In both cases the surfactant forms an insoluble complex with a non-surface-active molecule or ion and the product is floated out. To date almost all the work has involved flotation of ions using an oppositely charged surfactant. Sebba deserves special credit in the development of this process (*10*), with a book devoted to this subject (*11*). Undoubtedly the greater success in ion flotation in comparison to molecular flotation results from the fact that for the most part formation of ion-pair complexes is much stronger than dipolar complexes.

In the area of nonfoaming adsorptive bubble separation there are at present two categories—solvent sublation (*11*) and bubble fractionation (*12*). Solvent sublation involves the collection of the enriched material on the bubble surface in an immiscible liquid atop the bulk liquid media. This method would seem to hold promise in analytical separations as well as certain large-scale removal problems. A perfunctory examination would lead one to believe that this process is quite similar to solvent extraction; however, there are some notable differences which we shall enumerate. Bubble fractionation involves neither a foam nor a second immiscible liquid phase. In essence, the bubbles travel through an elongated bulk liquid medium and transport the surface-active material to the top of the liquid pool. A concentration gradient is thus set up, and the enriched top product can be collected by removal of the top section of the liquid pool. This process is especially effective for weakly surface-active materials or surface-active materials of low concentration. Lemlich has developed this process and his articles can be referred to for further details (*12,13*).

Besides the aforementioned book by Sebba (*11*), several reviews have appeared in the literature dealing with the field, excluding from our discussion the technique of ore flotation. Cassidy (*14*) reviewed the early literature in 1957. In the early 1960s, one can find good discussions of foam separation by Rubin and Gaden (*15*) as well as by Eldib (*16*). Recently Grieves (*17*) has reviewed his rather extensive work in the application of foaming techniques to the cleanup of waste waters.

FUNDAMENTALS

Surface-Active Materials

Now that the scope of adsorptive bubble separation methods has been discussed, it is important to understand the underlying princi-

ples common to all methods. We shall first examine the simple case of the separation or removal of surface-active species from aqueous media. Under equilibrium conditions, adsorption of species from a bulk solution at a gas–liquid interface can be quantitatively described by the Gibbs equation (*18*). If the interface is defined as a plane in which the concentration of the solvent is the same as in the bulk solution, and if we assume that concentration can be substituted for activity (i.e., dilute solution), then the Gibbs equation can be written as

$$\Gamma/c = -\frac{1}{RT}\frac{d\gamma}{dc} \tag{1}$$

where Γ is the surface excess of the adsorbed solute (i.e., the moles of solute per unit area at the defined interface in excess of the number of moles of corresponding unit area in the bulk solution), c the bulk equilibrium concentration, and γ the surface tension.

In essence, Γ/c can be considered a distribution factor, since it is a ratio of the concentration at the interface to that in the bulk solution. Since equilibration takes place between a two-dimensional surface and a three-dimensional liquid phase, the units on Γ/c are centimeters. In Eq. (1), it is seen that the distribution factor and thus the extent of adsorption depends on the negative slope of the plot of γ versus c. A hypothetical surface tension–concentration curve is shown in Fig. 2 for a species which will preferentially adsorb at the surface, e.g., sodium lauryl sulfate, ABS, etc. We see that there are essentially three regions of concern: one at very low concentration, ca. 10^{-6}–10^{-7} M or less, in which the slope is close to zero; a second of intermediate concentration in which the slope is a fairly constant value; and a third at higher concentration in which the slope again becomes close to zero. We shall now examine each of these regions.

At very low concentrations little adsorption can occur, since there are few surface-active molecules or ions present, and so the surface tension is close to that of the solvent, i.e., water. The distribution coefficient is then close to zero and separation occurs only to a small extent. It is worth pointing out, however, that this concentration can be quite low, e.g., 10^{-7} M or less.

At intermediate concentrations [between (a) and (b)], Γ decreases with increasing bulk equilibrium concentration; i.e., a negative slope occurs. Thus, from Eq. (1), Γ/c becomes greater than 1, and

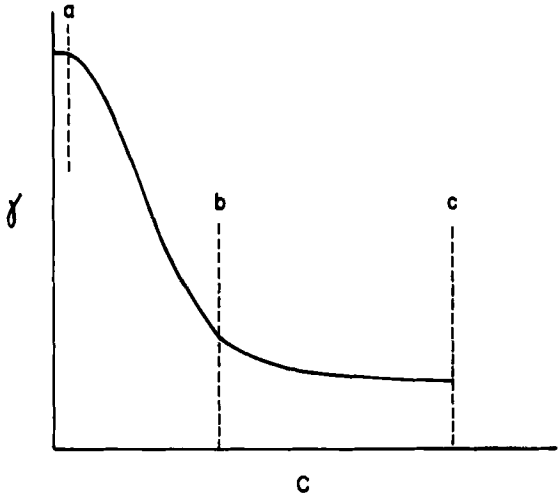

FIG. 2. Hypothetical surface tension, γ, versus concentration, c, plot for a surface-active agent in water. The sections a, b, and c denote specific subdivisions of the curve and these are discussed in the text.

selective adsorption of the surface-active species occurs at the gas–liquid interface. Often the functionality is linear over a portion of this region, and the distribution coefficient of the surface-active agent becomes constant, independent of bulk concentration. In any event, the distribution is such that separation of surface-active material from the bulk aqueous phase may be achieved using an adsorptive bubble separation method. Realizing that there may be examples of wide variation, we can say that, on the average, concentrations between ca. 10^{-6}–10^{-7} M up to ca. 10^{-3} M fall within this range for a number of surface-active species. It should also be recognized that processes involving the use of foams will require surfactant concentrations at the higher end of the scale, in order that a stable foam may be produced.

In the region above concentration (b) in Fig. 2, we see that the slope becomes constant, and indeed close to zero. This is the region in which micelles form, and the point at which the curve levels off is called the critical micelle concentration, CMC. According to the Gibbs equation, the distribution coefficient should become close to zero and no removal should occur in adsorptive bubble processes. However, in reality, foams are formed in the micelle region, and removals are successfully carried out. Thus one can operate foam

columns in the micelle region. It is worth pointing out, however, that better removals would occur below the CMC, as found by Newson (*19*) and others (*20*).

The question can be raised concerning the general applicability of the Gibbs equation to adsorptive bubble separation studies, i.e., whether equilibrium is actually achieved in these dynamic processes. The work of Newson is quite important in this regard, for he was able to show that surface excess values for surfactants measured by foam fractionation closely agreed with static measurements (*19*). Thus in the simple surfactant removal cases, equilibrium is probably closely approached at steady state. However, in more complicated systems involving several surfactant and nonsurface-active species, one must be very careful in assuming that surface–bulk equilibrium has been obtained. In any event the Gibbs equation can be used as a qualitative tool in understanding the separation process.

The above discussion has dealt with the removal of surface-active species from aqueous media by selective adsorption on bubbles. No matter what the method of collection of the enriched interfaces, the separation step will occur in the aqueous phase, and quite obviously, unless there is selective adsorption, no separation or removal will take place. Thus it is important to understand as much as possible the surface chemistry involved, i.e., the thermodynamics or kinetics of adsorption on mobile gas–liquid interfaces. It is not our purpose to go into this subject in this review; for the interested reader, excellent books are available (*21*).

A second aspect of the methods is their efficiency, i.e., how a separation developed by the selective adsorption process is improved by the separation system. In this area one must consider such subjects as reflux, drainage of foams, and column design. We shall cover these subjects shortly. The point we wish to make at this time, however, is that the adsorptive step is the essential one; efficiency is important, but without some selective adsorption, the efficiency is of little value.

Finally, it should be recognized that adsorptive bubble methods are basically separation processes for low-concentrated materials. From the Gibbs equation and Fig. 2, we see that the distribution coefficient actually improves with decreasing concentration as we pass the CMC. The low-concentration aspects of these methods will be emphasized later.

Non-Surface-Active Material

Exclusive of ore flotation, the early work in foam separation methods involved the separation and removal of surface-active species. However, through surface chemical studies, it became clear that non-surface-active species, especially ions, could be made surface active by attachment to surfactants. Thus surface-active ion pairs could be formed between an ion and an oppositely charged surfactant. The work of Walling et al. (22), among others, indicated that these species could be foamed. Since that work, a number of groups have applied this information to effect foam separation of non-surface-active species. For example, metals have been removed using anionic surfactants (23), organic bases using anionic surfactants (24), and anionic dyes using cationic surfactants (25). Also, nonfoaming adsorptive bubble separation methods have been used to remove non-surface-active species (26).

As previously, we can consider a distribution factor, Γ/c, as a measure of the selective adsorption step. This distribution factor should strictly apply only to the surfactant–solute complex species, whereas in actual fact the c that is measured is the total concentration of the solute (complexed and uncomplexed) in the bulk phase.

Figure 3 shows plots of the surface excess versus bulk equilibrium concentration of the non-surface-active solute and the distribution factor versus bulk equilibrium concentration. We see that at low concentrations Γ is proportional to c, and the distribution coefficient is thus independent of concentration. Beyond a certain concentration, however (ca. 10^{-7}–10^{-5} M), Γ becomes constant, independent of concentration, and the distribution factor thus decreases with increasing concentration. Presumably in this region, the surface has become saturated with the solute, so that additional solute must remain in the bulk phase. The behavior illustrated in Fig. 3 has been confirmed by Banfield et al. (27), Rubin (28), and Karger et al. (29), among others.

The simple model describing this behavior can be either thermodynamic or kinetic. In the thermodynamic approach, one considers the gas–liquid interface as a mobile ion-exchanger. In the overall result it does not matter whether the surfactant–solute ion-pair complex forms at the interface or in the bulk phase; however, the picture is one of exchange at the surface. If we consider the solute

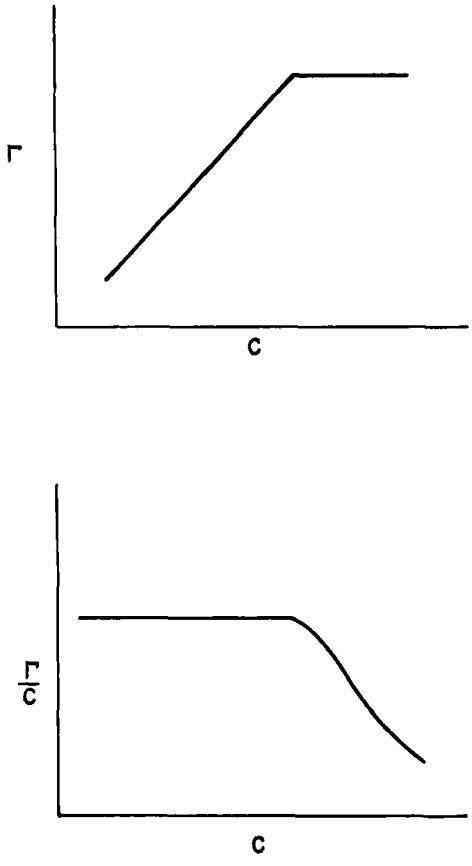

FIG. 3. Hypothetical plots of distribution coefficient, Γ/c, versus concentration, c, and surface excess, Γ, versus c in a foam separation process. The example is for a case of a non-surface-active species complexing with a surfactant and being subsequently removed in a foam.

being removed as a univalent anion using a cationic surfactant and that this solute exchanges with chlorine ions from the surfactant, then the exchange reaction can be written as

$$(S^-) + (Cl^-)_S \rightleftharpoons (S^-)_S + (Cl^-)_b \tag{2}$$

where S^- denotes the solute and subscripts b and S the bulk and surface phases, respectively. The exchange constant is then

$$K_{ex} = \frac{[S^-]_S[Cl^-]_b}{[S^-]_b[Cl^-]_S} \tag{3}$$

The K_{ex} value will depend, of course, on the relative affinities of (S^-) and (Cl^-) for the cationic surfactant and their relative solubilities in water. The concentration at the surface is just

$$[S^-]_s = \frac{\Gamma_{S^-}}{d} \qquad [Cl^-]_s = \frac{\Gamma_{Cl^-}}{d} \tag{4}$$

where d is the thickness of the defined interfacial layer. Equation (4) may be substituted into Eq. (3) to give

$$\frac{\Gamma_{S^-}}{[S^-]_b} = K_{ex} \frac{\Gamma_{Cl^-}}{[Cl^-]_b} \tag{5}$$

Equation (5) indicates that the distribution factor of S^- should be proportional to the distribution factor of Cl^-. In the concentration region in which the distribution isotherm is linear, the distribution factor of the chloride ion must be constant. This result means that $\Gamma_{Cl^-} > \Gamma_{S^-}$ or that the surface is covered to a great extent with chloride ions. Often the bulk concentration of the chloride ion will be maintained constant, or, at the very least, $[Cl^-]_b$ will be constant when the distribution isotherm is linear. At higher concentrations the surface becomes saturated with S^-, and Eq. (5) cannot be applied without modification. Using simple algebra, however, modified expressions can easily be obtained (*29*).

We see from Eq. (5) that the extent of removal of a non-surface-active species can be controlled by several factors. In the first place the higher the concentration of ions other than the solute (i.e., the higher the ionic strength), the lower will be the removal (*30*). In essence these ions will compete with the solute for the cationic sites on the surface.

Second, we can control the extent of removal by the concentration of the solute species in the system. Thus, for example, we may remove anionic chloro complexes of metals using cationic surfactants in high concentrations of hydrochloric acid (*31,32*) in much the same manner as has been done by Kraus and Nelson in ion-exchange chromatography (*33*). The concentration of the hydrochloric acid, and thus the chloride ion, will control the extent of formation of the anionic chloro complex (*29*).

$$\frac{\Gamma}{C} = K_{ex} \frac{\Gamma_{Cl^-}}{[Cl^-]_b} K_f [Cl^-]_b^n \tag{6}$$

where K_f is the formation constant of the chloro complex and n is

the number of chloride ions in the complex. The chloride ion concentration can thus control the extent of removal of the metal ion.

This effect can also be used for selective removal of one metal species over another. Thus a chloride ion concentration could be selected in which one metal complex forms but not another. Since the cationic surfactant only attracts the anion, separation of the metal species can be achieved. For example, at 1 *N* HCl concentration, Hg^{2+} forms a strong anionic chloro complex, whereas many other metal ions, such as Fe^{3+} and Co^{2+}, do not. Mercury can thus be separated from these other metals at 1 *N* HCl (*32*). Clearly this approach can be applied to many other types of complexes. It is worth pointing out that the information developed for separation in ion exchange using this approach can be directly applied for prediction of separation in adsorptive bubble separation processes.

Finally the extent of removal will depend on the exchange constant K_{ex}. In essence this constant will be a measure of the ability of the non-surface-active species to complex with the surfactant. The more favorable the formation of the ion pair, the better will be the removal. Thus it has been found that surfactants which can act as chelating agents as well as exchange sites will more readily remove metal ions than simple charged surfactants (*34*). Presumably selectivity can also be incorporated here for removal of one species in the presence of the other species. More work needs to be done in the exploration of different types of surfactants for removal of non-surface-active materials. It is our feeling that this would be a fruitful area for investigation.

The second model that may be used to describe the removal of non-surface-active species is a kinetic one involving the Langmuir isotherm. Here we are concerned with the rates of adsorption and desorption of the solutes from the surface phase. The resultant equation is (*28*)

$$\frac{\Gamma_{S^-}}{[S^-]_b} = \frac{K_1 K_2}{1 + K_1[S^-]_b} \tag{7}$$

where K_1 and K_2 are constants. At low concentrations of $[S^-]_b$, $K_1[S^-]_b << 1$, and the distribution factor becomes constant, equal to K_1K_2, in agreement with Fig. 3. As $[S^-]_b$ increases, the denominator in Eq. (7) no longer equals unity, but increases such that the distribution factor will become smaller, again in agreement with Fig. 3. A rather good discussion of this model, including an experi-

mental determination of K_1 and K_2, can be found in Rubin's Ph.D. thesis (28).

Measurement of Distribution Factors

Experimentally, distribution factors for foam separation can best be measured using a closed system in which the collapsed foam liquid is recycled to the bulk solution. In this case we continue the recycling process until a steady state has been achieved, as evidenced by the constant concentrations of material in the liquid from the broken foam and the bulk medium.

A foam consists of two regions of liquid material—one at the gas–liquid interfacial surface and the other in the spaces between foam bubbles, i.e., the Plateau borders. Enriched material will exist at the surface of the bubbles as a result of selective adsorption. However the Plateau borders will contain material at a concentration similar to the bulk liquid (assuming no reflux) due to the fact that bulk liquid is trapped as the foam is formed.

Let C_F represent the foamate concentration, C_B the bulk liquid concentration, L the collapsed liquid flow rate, G the gas flow rate, and S the specific surface area (total area of surface per unit volume of foam). If it is assumed that the concentration of the interstitial liquid in the foam is the same as the bulk liquid concentration, then a material balance equation can be written as

$$C_F L = C_B L + \Gamma G S \tag{8}$$

Rearrangement gives

$$\frac{\Gamma}{C_B} = \frac{L}{GS}\left(\frac{C_F}{C_B} - 1\right) \tag{9}$$

Now $C_F/C_B = E$, the enrichment ratio, and $S = 6/D$ for spherical bubbles and $6.59/D$ for regular dodecahedra, where D is the foam bubble diameter. For spherical bubbles the final equation is then

$$\frac{\Gamma}{C} = (E - 1)\frac{LD}{6G} \tag{10}$$

The factors G and L in Eq. (10) can be directly measured, along with direct analysis of the foamate and bulk concentrations.

The major problem in accurate determination of the distribution factor resides in the measurement of the foam bubble diameter.

Our procedure involves photographing at the column wall through a magnifier onto Polaroid slide projector film. By photographing an accurate scale as well and projecting both films, it is possible to obtain an estimate of the bubble diameter. It is altogether possible that the number obtained is not the true diameter since bubble distortion will occur on the glass walls of the column. (Photographic distortion can be minimized using a flat optical plate at the column wall at the point the picture is to be taken.) Banfield et al. (27) photographed the bubbles from above the column; however, the distortion problem arises here as well, since the pressure on the top bubbles differs from that in the center of the column. We feel that at present there is no acceptable method available for good bubble measurements and that this is an area well worth exploring.

Two other points should be made in this regard. First, the distribution of bubbles should be as narrow as possible, and, second, at least 100 bubbles should be measured. For the first case we have found that a spinnerette is far superior to a glass frit as a sparger. We shall discuss the type of sparger in a later section. The bubble diameter that is used in Eq. (10) is, of course, an average diameter, obtained from a volume-to-surface-area ratio:

$$D = \frac{\Sigma\, n_i D_i^3}{\Sigma\, n_i D_i^2} \tag{11}$$

Equation (10) relates the enrichment ratio, E, to the distribution factor. If one is operating a column as an enricher, then E is the parameter of concern. However, E depends on foam characteristics, i.e., the wetness of the foam, the bubble diameter, etc., and if one wishes to study foam–liquid equilibrium, the distribution factor should be used. The functionality, $E - 1$, in Eq. (10) is such that errors in E are magnified when E is close to 1. Small E values arise from poor adsorption and/or wet foam. There is little we can do about the first factor, but we surely can attempt to keep the foam fairly dry. Of course there are limits to the dryness of the foam, for a stable foam must be used.

A second approach for measurement of Γ/c has been used by Banfield et al. (27). In this case the material is continuously fed into the bulk liquid, and the foam is continuously collected along with bulk residue. The steady state is achieved in the continuous-flow system. This approach has value for large-scale studies; how-

ever, the reproducibility is considerably poorer than the closed system approach, previously described.

MODES OF FOAM OPERATION

In foam separation processes, there are a variety of techniques that can be used for operation of the foam column, depending on the problem that must be solved. Figure 4 presents in diagrammatic form many of the possibilities that are available. Clearly the simplest procedure is to take a batch system, generate gas bubbles in the media, and collect the foam that is produced. For a large-scale process this approach is not feasible, and so instead, as shown in Fig. 4, the bulk liquid is fed in a continuous manner, the gas is bubbled, and the foam is collected overhead with the bulk residue collected below.

If we wish to concentrate material in the foam layer, i.e., use the foam column as an enricher, it is necessary to perform reflux. In reflux the collapsed liquid from the foam is recycled (either partially or totally) into the foam column. Again the feed may enter the bulk liquid. We shall discuss reflux in more detail in the next section.

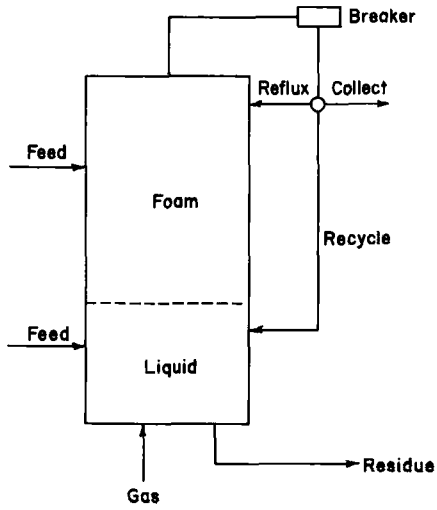

FIG. 4. Schematic representation of several of the various modes of operation of a foam column. The several modes are discussed in the text.

In a third case, we may wish to operate the foam column as a stripper by feeding the sample directly into the column, as shown in Fig. 4. In this mode the bulk liquid contains sufficient surfactant concentration to maintain a foam column. Presumably the floatable material is carried over in the foam, and the residue travels out the bulk liquid end. If desired, this floatable material could be concentrated by reflux operation. In the latter mode the column is combined as a stripper and an enricher type. Finally, in Fig. 4, we show a recycle possibility, for use, as noted previously, for foam-liquid equilibrium studies.

Reflux

As we have said, a foam consists of enriched material on the surfaces of gas bubbles along with bulk liquid entrapped between the bubbles in the Plateau borders. For surfactants, the rapid rate of adsorption along with the rapid mixing from convection probably means that the bubble surfaces are fairly saturated when the foam is formed. Thus the limiting factor in concentrating surface-active species in a foam is the entrapped bulk liquid.

For enrichment to be improved in the foam, one of two things must occur, either the entrapped liquid must be drained from the foam or the entrapped liquid must become enriched with the material that is to be removed. Film drainage in foams is a complex phenomenon, requiring detailed mathematical descriptions. In this qualitative review it is not our purpose to cover this topic. For the interested reader the best development has been by Lemlich and co-workers (35–37). The wetness of a foam can be controlled in the main by the gas flow rate (i.e., slow rates give dry foams), type of sparger, column design, and temperature.

One is somewhat limited in using drainage since foam stability requires that the foam not be completely dry. A more fruitful method would appear to be reflux in which the entrapped liquid is enriched by the recycling of the foamate into the foam. Reflux has the added advantage that in those cases of foam separation of non-surface-active materials in which the surface of the bubble is not saturated with the material as the bubble leaves the bulk medium, saturation may take place in the foam. Lemlich and Lavi (38) were the first to show the value of reflux in 1961. Eldib (39) and Lemlich and co-workers (*37,40*) have further examined reflux for foam separation.

We have also been interested in reflux as a means of concentrating trace quantities of material on an analytical scale (*25,41*). Using a batch system, the procedure has involved total reflux for a given period of time, followed by an appropriate collection procedure. In total reflux the foam is broken at the top of the column and the total liquid is allowed to flow over lower layered bubbles. The breakage is ordinarily accomplished by passing steam through a Friedrich's condenser placed on top of the foam column. The heat breaks the foam with very little loss in liquid due to evaporation. After the reflux period, cold water may be passed through the condenser in order to allow passage of the foam to the collector section. Using this approach, we have been able to concentrate dyes, metal chloro complexes, and organic bases by a factor of 100–200. If the material is heat sensitive, a mechanical foam breaker can be used, such as a spinning wire basket. Such species as vegetable lecithin have been concentrated and recovered by this procedure (*25*).

By far the most important contribution on the large-scale level employing reflux has been by Schonfeld and Kibbey (*3*). They used controlled reflux for the removal of radioactive strontium from nuclear waste streams, in which the column was operated in a continuous stripping mode. The reflux ratio was controlled by a clever funnel arrangement employing an electromagnet to tilt the funnel in the proper direction. In this system the decontamination factor was in excess of 10^3 and the volume reduction (feed volume per foamate volume) was as high as 3700. The volume reduction factor is important in waste removal problems, and without reflux the value was found to be only 30. The feed rate was maintained at about 40 gal/ft^2 of column cross section per hour. The apparatus described in this article is a significant advance in the waste removal field.

Equipment

A word or two is in order concerning the equipment in a foam system. A particularly good discussion of this subject can be found in an AEC contract report by Haas (*42*). The gas sparger can be basically of three types: (a) capillary, (b) spinnerette, or (c) glass frit. For fundamental studies a capillary bubbler is most desirable, since large gas bubbles can be generated which are easily measured. The problem arises, however, that in order to produce a stable foam for measurement of distribution factors, it is often

necessary to use several capillaries together. From experience it is apparent that the internal diameter of the capillary as well as its length must be closely controlled to produce bubbles of uniform size. The task becomes an extremely difficult one to match the capillaries.

The porous glass frit has been successfully used in our laboratory in a number of applications. In this case numerous small bubbles are generated from the plate, and a wet and stable foam is produced. A coarse porous glass frit is the sparger of choice for separation applications, especially on a large-scale basis. However, for fundamental adsorption studies involving the distribution factor, the glass frit should not be used because the bubble size in the foam is quite variable. The difference in bubble diameters can be as much as a factor of 4 or 5 from the smallest to the largest.

We have found the spinnerette to be most satisfactory for measurement of distribution factors in foam separation. Using a 30-hole, 89-μ spinnerette, stable foams are obtained in which the bubble diameter varies by only 15% from the smallest to the largest (29). The foam obtained is much drier than that from a porous glass frit, and so the enrichment factor, E, is larger, resulting, as noted previously, in better precision in Γ/c. In general the bubbles are pentagonal dodecahedral in shape, as contrasted with the spherical bubbles from the glass frit. Again it should be emphasized that when foam separations are being used, especially on a large scale, a coarse porous glass frit is the sparger of choice.

To maintain a dry foam for enrichment purposes, it is useful to employ a long column, so that a good deal of drainage can take place. In general cylindrical columns are used; however, other shapes have also been recommended. To promote drainage, an expanded head section has been placed at the top of the column in certain cases (*15*).

Finally, in certain applications it is necessary to break the foam, after its exit from the column. It should be emphasized that in a simple foam separation, it will probably be acceptable to collect the foam directly in a container and then collapse the foam, perhaps by cooling to 0°C. However, for foam equilibrium studies and the use of reflux, a foam breaker is necessary.

The design which we have found to be most successful is a spinning basket made up of stainless steel wire mesh. The foam travels into the basket and is thrown to the sides by the centrifugal

force field. The foam bubbles then collapse on the wire mesh, probably as a result of some shearing action. Often a metal plate is placed on the bottom of the basket for balance as well as for prevention of foam escaping through the bottom. Efficient foam breakage occurs at ca. 1000–1500 rpm. The dimensions of the basket will obviously be a function of the quantity of foam to be broken. For corrosive materials, such as HCl, we find that a polyethylene wash bottle in which small holes are punched works satisfactorily. For those that are interested, Rubin has a particularly good description of the spinning basket foam breaker in his Ph.D. thesis (*28*).

Recently Goldberg and Rubin have recommended the use of a spinning teflon disk for foam breakage (*43*). We have tested this design in our laboratory and find it not to be as satisfactory as the spinning basket. Also, Haas (*42*) has recommended drawing the form into an evacuated chamber for breakage. Unfortunately, we have had no experience with this design.

APPLICATIONS

Now that we have discussed the fundamentals of adsorptive bubble separation processes, it is important to explore some of the more important applications and suggest areas of potential application. In this discussion it is not possible to detail all the areas of use, and we shall of necessity be quite selective. It is hoped, however, that the reader will obtain some indication of the more important applications. We shall leave aside discussions of ore flotation since this is covered in many other sources (*1*).

Water Waste and Nuclear Waste Treatment

Foam separation methods are basically large-scale processes in which removals of trace quantities of materials are effected from aqueous media. It was thus natural that these methods be applied to the cleanup of polluted streams. Major pollutants a few years ago were ABS and other hard detergents. Foaming of these detergents seemed a simple procedure for their removal (*44*). A pilot plant was set up in California and allowed to operate for several years. Economic studies were performed and the process was found to be inexpensive, since the surfactant was already present in the water (*45*). As an added bonus, other pollutants, both organic and inorganic, were found to be carried out with the foam.

With the changeover to biodegradable detergents, removal of ABS was no longer a pressing problem. Nevertheless, adsorptive bubble separation processes still offered potential in certain specific problems related to the cleanup of industrial waters. Interest thus turned to the removal of non-surface-active species, such as dichromate (*46*), phosphate (*47*), and phenolate (*48*). Grieves has summarized his extensive work in this area in a recent review article (*17*) and has indicated that successful removals of the above species and others are possible in the ppm range. Also, studies were undertaken for removal of microorganisms (*7*) and clays (*8*) for water clarification. We shall have more to say shortly on microflotation and colloid flotation.

It would appear that adsorptive bubble processes are most suited to inplant treatment methods of industrial wastes. As a surfactant must be added to remove the non-surface-active species, the cost of the process is greater, of course, than in the case of the simple removal of ABS. Nevertheless, the ability to recover the waste products for reuse should be appealing. Likewise the surfactant may be regenerated for reuse in the treatment process. Thus the cost factor need not be unreasonable. Continuous removal and recovery of trace pollutants from industrial wastes at an economic level provide a great deal of potential for these methods. In general synthetic waters have been used up to the present time; pilot plant studies on industrial waste cleanup would now appear to be in order.

In the nuclear waste field, a good deal of interest was shown several years ago in the removal of trace radioactive metals by foam separation (*23,34,42*). Effective removals of such isotopes as ^{89}Sr and ^{90}Sr were achieved. The major drawback appeared to be the volume reduction factor of only 30–40. With the emergence of the reflux apparatus of Schonfeld and Kibbey (*3*), previously described, volume reduction factors as high as 3700 were possible. At this level, foam separation would appear to be competitive with more conventional waste treatment procedures. However, with the cutback in funding for the AEC, the further development of this method seems to be stalled in this country. The Atomic Energy Establishment at Harwell has continued studies in this area (*27*); however, even here interest has diminished in the use of this method for waste removal.

Biopolymeric Applications

The application of foam separation to the purification and concentration of enzymes and other proteins is particularly attractive. By nature, proteins such as enzymes are subject to denaturation by heat and mechanical shearing, and thus the methods of separation of these delicate materials are limited. Chromatography, ion exchange, and liquid–liquid extraction are the methods routinely employed in the separation and purification of proteins. These methods are quite satisfactory for separation and purification of small quantities of material but timewise they are inadequate for larger volumes of protein mixtures. To obtain a large quantity of purified material often requires up to several days if a method such as column chromatography is used. Being naturally surface active, proteins lend themselves nicely to foaming methods. Foaming is a very mild process and in the case of enzymes it has been found that very little if any denaturation results during the separation in most cases tested. The advantages of high volume capacity, mildness, speed, and, in many instances, specificity make foaming very attractive on a preparative scale. A survey of the literature shows several interesting applications of foaming in the purification and separation of proteins and enzymes.

The early work in this area dealt with a somewhat qualitative fractionation of biopolymers. For example, Ostwald and Siehr used foaming to separate albumin from potato and beet juices (*49*). In a more detailed study, Schütz foam fractionated methylcellulose according to molecular weight and methylation (*50*). Bader and Schütz also applied foaming to enzyme fractionation (*51*).

In the mid 1950s London and co-workers (52) studied the application of foam fractionation to the purification of mixtures of two enzymes—urease catalase. The effects of protein concentration, pH, salts, and the addition of ethanol were investigated. When a mixture of urease and catalase was foamed, a preferential enrichment of urease in the foam was observed, while most of the catalase remained in the bulk. London attributed this selective concentration in the foam to the difference in surface activity between the two enzymes; i.e., urease is more surface active than catalase. The highest purification and recovery of urease and catalase occurred near the isoelectric point. Recoveries of over 75% were routinely

achieved and under optimum conditions recoveries close to 100% were found.

Results somewhat similar to London's work were obtained by Schnepf and Gaden (53) in the foam fractionation of bovine serum albumin (BSA). The surface tension–concentration curve of BSA showed the greatest negative slope at the isoelectric point. Thus the greatest enrichment of BSA in the foam occurred at the isoelectric point. Using an aqueous solution only 0.0002% by weight in the BSA, a stable foam was produced when the solution was sparged. Enrichment ratios as high as 20-fold were obtained.

Charm and co-workers, at the New England Enzyme Center, are currently using foam fractionation to purify and concentrate the enzymes amylase and catalase (54). The difference in surface tensions of these two enzymes results in a preferential concentration of catalase in the foam, while amylase is concentrated in the residual bulk. Note that in the study by London et al. (52) catalase was concentrated in the bulk, which is the opposite to what Charm has achieved. The reason for these opposite results lies in the relation of the surface activities for the components in a solution. For two components the solute exhibiting the higher surface activity tends to concentrate in the foam. Charm et al. also found a salting-out effect in that the addition of ammonium sulfate increased the concentration of catalase in the foam.

Recently, Charm and Potash (55) have used foam fractionation to concentrate and purify lactic dehydrogenase (LDH). When a mixture containing LDH and several other more surface-active proteins is foamed, LDH is concentrated and purified in the residual bulk, while the other components are removed in the foam. Up to a threefold purification of LDH, determined by its specific activity, was observed, though the average was a twofold purification. The useful effect of ammonium sulfate on the foam purification of LDH is shown in the data of Charm and Potash (55) on p. 415.

In column chromatography Charm finds that up to a sevenfold increase in specific activity is possible using LDH; however, and this is the key point, the chromatography is quite slow, of the order of days. The threefold increase observed in foaming requires less than $\frac{1}{2}$ hr. There is thus a substantial saving of time. Preparation of small amounts of purified protein or enzyme may not require consideration of the time factor; however, in large-scale purification time is money. Thus it may well be that foam fractionation can be-

Initial spec. act.	Residual spec. act.	% $(NH_4)_2SO_4$
15.3	31.0	0
22.6	33.2	0
26.0	107.0	20
41.4	104.0	20
45.2	92.5	30

come a useful process for preparation of large amounts (on a relative scale) of purified biopolymers. Certainly, investigations directed along these lines would be quite profitable.

Microflotation and Colloid Flotation

The flotation of microorganisms is an application of adsorptive bubble processes which is relatively old. In 1941, Dognan and Dumontet collected tubercle bacilli in the foam of the surfactant naturally produced by the organism (*56*). Boyles and Lincoln in 1959 (*57*) separated bacterial spores and vegetative cells by foaming. Others active in the field were Hopper and McCowen (*58*) and Gaudin et al. (*59,60*).

Rubin et al. (*4*) have recently successfully floated *E. Coli* and several species of algae. Contrary to the previous work they used low gas flow rates for more efficient removal (i.e., a drier foam). Flocculents, such as alum, and frothers, such as ethanol, were also found to aid removal. Rubin also removed *Aerobacter aerogenes* using both anionic and cationic collectors (*61*). Grieves et al. have also been active in this area (*7,62,63*). Even with this activity, Rubin has stated that "At the present time there is no way of determining *a priori* the extent to which a particular microorganism will adsorb a specified collector." The mechanism of removal is thus not at all clear and more work should be done in the area.

The flotation of microorganisms is of value for several reasons. First, using high gas flow rates, removal rates are much more rapid than the other separation processes often used. Second, the foaming process can be important in water pollution control, for the removal of bacteria from dilute suspensions will allow reductions in disinfectant dosages. Third, foaming can provide a means of concen-

trating cells for more accurate cell count analyses. Finally, an understanding of the mechanism of removal should indicate fundamental surface phenomena related to the microorganisms. Thus, microflotation of species such as bacteria is well worth pursuing.

Colloid flotation is another method worthy of mention. In this case colloidal materials, other than microorganisms, are removed by a flotation process. The usual method of removal of colloidal material from aqueous media involves a coagulation step and then a settling step. Flotation may offer a second avenue of approach, especially for those colloidal systems which are difficult to coagulate.

With the extensive work performed in ore flotation, it is not surprising that colloid flotation was studied at a rather early stage. In 1938 Clanton and Magoffin floated ferric oxide, aluminum oxide, and chromic oxide sols (*64,65*). Hopper and McCowen were among the first to propose flotation for turbidity removal (*58*). Note should also be taken of the extensive work by the Russians in the flotation of colloidal particulates (*66–69*).

Grieves has applied colloid flotation in the water clarification of low-quality waters available for small communities or for military use in the clarification of field water supplies (*70*). Starting with a suspension of natural dirt and sand, Fuller's Earth, and Illite clay, with an initial turbidity of 125 Jackson candle units, the effluent turbidity was less than 10 units after foaming. In a later publication (*71*), Grieves and Crandall further established the feasibility of using foam separation for the clarification of low-quality water. The investigation showed that a suspension containing six clay and sand constituents and minimal concentrations of iron and aluminum could be clarified at the rate of about 3 liters/min for 30 min with a dosage of only 30 mg/liter, in four additions, of cationic surfactant. It may be noted that natural clays, such as kaolinite and montmorillonite, are anionic so that cationic surfactants are needed for the flotation process. On the other hand, for species such as ferric oxide sols that are positively charged, anionic surfactants should be used (*72*).

Grieves has studied a number of variables involved in the flotation of colloids. These include gas flow rate, pH, and added electrolyte. It has become clear that an important and perhaps determining factor in the flotation of colloids is the charge on the colloid. This charge depends on the inherent structure of the colloid as well as certain properties of the medium such as pH and ionic

strength. These properties of the medium can thus play an important role on the removal of the colloid.

Bikerman has shown that foam stability is greatly enhanced when particulates are in contact with air bubbles (*73*). Grieves and Schwartz have also found this in their work (*46*). Thus the colloid will act as a frother itself and will eliminate the need for addition of a species, such as ethanol, as Rubin and Johnson found necessary in certain of their studies (*74*). This frothing action of the colloid also means that foams may be produced with smaller amounts of surfactants.

Adsorbing colloid flotation, an offshoot of colloid flotation, is a completely unexplored area that may have potential for removal of trace non-surface-active or weakly surface-active ionic species from aqueous media. In this technique the ionic species are first adsorbed onto the colloid and then the particulates are subsequently removed by flotation. The adsorption step most probably occurs by an ion-exchange mechanism. It should be pointed out that in the flotation of a colloid itself, adsorbing colloid flotation actually occurs, since the surfactant is removed by adsorption on the colloid. Without perhaps realizing it, Grieves also applied adsorbing colloid flotation in one study in which bentonite was added to water to remove interfering ions in the flotation of kaolinite (*70*). The bentonite adsorbed the ions and removed them from the solution in the flotation of this clay. An approach similar to adsorbing colloid flotation was also applied in the extraction of trace concentrations of radioactive isotopic metal ions (*75*) in which over 99% of the metal was removed.

It is interesting to speculate on the comparison of adsorbing colloid flotation to ion flotation. The former technique may be more efficient for removal of ions for the following reasons. First, the surface area of the colloidal particulates can be quite high, especially for clays, e.g., 5.8 m^2/g for kaolinite and 71.0 m^2/g for montmorillonite (*76*). A number of colloidal particles should attach themselves to each bubble as flotation proceeds. Thus, if for simplicity we think in terms of an ion-exchange mechanism, the number of exchangeable sites per bubble should be greatly increased in adsorbing colloid flotation over that which can occur in ion flotation, since exchange can take place on the colloidal particles as well as at the simple gas–liquid interfacial surface. Thus it may be that adsorbing colloid flotation is inherently more efficient than ion

flotation, even taking into account that some of the sites on the colloid particles will be taken up by surfactant molecules in the flotation process. Second, as already mentioned, colloidal particulates improve foam stability. Thus less surfactant may be required relative to ion flotation. It must again be emphasized that this comparison is only speculation at the present time. Experimental work must be performed to check these ideas.

SOLVENT SUBLATION

Solvent sublation is a nonfoaming separation method in which the gas bubbles deposit their enriched material in a liquid layer, such as 2-octanol or anisole, which is immiscible with the bulk aqueous phase. First suggested by Sebba (*11*), this technique has been investigated in detail only by Karger and co-workers (*26*, *77*,*78*); also, Davis (*79*) made some unsuccessful attempts at applying the method to trace metal separations.

As with other adsorptive bubble separation processes, solvent sublation is an effective separation tool for trace concentrations. Indeed, since a foam is not required, lower concentrations of surface-active species can be used in this process relative to the foam methods. The method would appear to have a definite role in trace analytical separations and a potential for large-scale industrial processes.

Results to date have indicated that there are several modes of extraction across the liquid–liquid interface, considering the removal of non-surface-active ions from aqueous media using oppositely charged surfactants. In the first place, there is the usual adsorption in the aqueous phase of the complex ion pair at the gas–liquid bubble interface and its subsequent removal into the nonaqueous layer. A second mode of removal involves the dragging of bulk water across the liquid–liquid interface into the nonaqueous layer. Miller (*80*) has recently obtained photographic evidence for this effect. In effect, this process is similar to the case in which bulk water is entrapped between gas bubbles in a foam column; however, the amount of water crossing the liquid–liquid interface is considerably less than that in foaming. Thus the inherent capabilities of solvent sublation for selective removal are greater than in foam separation.

Since the organic phase has been previously saturated with

water, the entrapped water droplets travel to the top of the immiscible layer and then back down into the aqueous layer. In effect, this mode provides for liquid–liquid mixing, so that after a long bubbling time, liquid–liquid equilibrium is established. Elhanan and Karger have shown that equivalent results are obtained for the solvent extraction of $FeCl_4^-$ with tri-*n*-octylamine into anisole and the solvent sublation of the same system for a 3-hr gas bubbling period at a flow rate of 20 ml/min (*78*). It should be pointed out that this effect is not a result of severe agitation of the liquid–liquid interface, since this interface is maintained stable at all times.

The important point to recognize, however, in a comparison of solvent extraction and solvent sublation is that in the shaking procedure liquid–liquid equilibrium is rapidly attained, whereas in the gas bubbling procedure longer periods are ordinarily necessary for equilibrium to be attained (*78*). Advantage can be taken of the slow extraction rate in solvent sublation for separation purposes. Thus, two species may be removed from the aqueous phase at significantly different rates, such that separation may be achieved by sublating for a specified period of time. This controlled time concept was used in the previously published separation of rhodamine B and methyl orange (*77*). The two dyes were found to separate much better at short times than at long times. Thus a separation factor of 56 was achieved in 15 min, while it decreased to 6 after 180 min sublation time. It may be further pointed out that the slow rate of removal can be of use in understanding the mechanism of sublation. It must also be recognized that there is flexibility in the rate of sublation by control of the gas flow rate and the type of sparger used (*77*). It is obviously possible to create liquid–liquid equilibrium in a rapid manner by fast flow rates, if that is desired.

Another interesting feature of solvent sublation is that the volume of the organic phase does not seem to affect the rate of removal of components, at least if we are not close to liquid–liquid equilibrium (*77*). Thus it is possible to place a thin layer of organic phase on top of the aqueous phase and still achieve good removals of material. This characteristic of the method should be of value in concentration problems both of an analytical nature and on a larger scale. In the latter case, one can conceive of continuously flowing a thin layer of organic solvent across a bulk water supply

through which gas bubbles travel. The material from the gas bubbles would then be deposited in the organic layer, which is collected in an appropriate manner.

Solvent sublation is a simple and inexpensive process to operate. Indeed, since a foam is not required, less surfactant is needed in this method relative to foam separation. Further details can be obtained by the interested reader from the cited references. Certainly this method is worthy of continued investigation, both on an analytical and large-scale level.

CONCLUSION

It is appropriate to compare the adsorptive bubble methods with other separation methods currently in use. Of necessity we must attempt to speak in general terms. The major use of the adsorptive bubble methods at the present time would appear to be the large-scale removal of trace quantities of material from aqueous media. Such removals can often be achieved at low cost. Chromatographic methods, such as ion exchange and column adsorption, have also been applied to such problems; however, they often do not work as well at low concentrations as the foam methods, simply because the capability for concentrating the sample is not as great, especially for column elution procedures. Likewise column chromatography would probably be hard pressed to compete on a time basis, and indeed throughputs have been estimated to be 10 times greater in foam separation relative to ion-exchange column chromatrography. It is worth pointing out that the throughput of foam fractionation may be low due to the use of interfacial surface for separation. However, as we have noted, the throughput of the flotation process need not be low.

Adsorptive bubble separation methods are performed at room temperature, so that heat-sensitive materials can be separated. Thus these processes may find value for systems in which methods, such as distillation or preparative scale gas chromatography, cannot be used. Foam methods are especially mild, and, indeed, workers have found that for a number of enzymes flotation does not diminish the activity of the enzyme.

One major disadvantage for adsorptive bubble separation methods at the present time is the lack of design of multistage columns. It is known that given two surface-active materials,

foaming in a series of columns will aid separation (*28,81*), and of course this result is due to multiequilibration. However, while several attempts have been made, no competent design has been developed to perform the same task in a single column (i.e., breaking and reformation of a foam in a single column). Thus, foam separation methods are based for the most part on single-stage processes, especially when the feed is placed into the bulk liquid. Several equilibrations are possible when the sample is fed into the foam column directly. One of the major problems with achieving multicontact in a single column is the holdup of bulk liquid in the column. Thus, filling the column with a packing, such as Raschig rings, will actually harm separation due to the prevention of drainage.

On the analytical scale, we have seen that solvent sublation can be a competitive process to solvent extraction. Indeed, the control of the separation by kinetic factors offers several advantages for solvent sublation. Among these is the fact that the volume of organic phase above the water does not in general influence the rate of extraction or the amount extracted in a given time period.

In the future, we see further development of some of the newer adsorptive bubble methods such as solvent sublation and adsorbing colloid flotation. The possibility exists for the use of one or several of these methods in mining the sea. Further advances will also occur in the preparation of biopolymers and microorganisms.

In this article we have attempted to present an overview of the adsorptive bubble separation field. Many of the techniques are relatively new, as well as a number of the applications. Nevertheless, a good deal of work has been accomplished over the last 8–10 years. Within the confines of this article it has not been possible to cover all these topics. We hope, however, that the reader has obtained a general view of the current state of adsorptive bubble separation methods.

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