

ADSORPTIVE BUBBLE SEPARATION METHODS

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TO MOST ENGINEERS, the adsorptive bubble separation methods [1,2] are a largely unfamiliar group of techniques. This may be due in part to the fact that these techniques are intimately based on surface phenomena. Most engineers seem to be more comfortable when dealing with bulk phenomena than with surface phenomena. Such a preference can prove awkward when an investigator or designer is faced with certain classes of problems.

The adsorptive bubble separation methods involve selective adsorption or attachment at the surfaces of bubbles rising through a solution or suspension. If the material to be adsorbed or attached, which is termed the colligend, is not surface active, a suitable substance called a collector may be added to unit with the colligend to form a surface active sublance which is carried up by the bubbles.

Prominent among these techniques, either in terms of application or research interest, are the flotation of particulate matter in wastewater treatment and in mineral beneficiation [ore flotation] [3], the foam fractionation of dissolved or fine colloidal matter [4], the collector-required technique of ion flotation [5], the precipitate-required technique of precipitate flotation [6], the foamless technique of bubble fractionation [7] which capitalizes on the vertical concentration gradient that is established in a vertically-elongated bubbled pool of liquid, and the foamless technique of solvent sublation [5] which makes use of an immiscible auxiliary liquid atop the main pool to entrap the adsorbed material from the existing bubbles. For the sake of brevity, the term adsorptive bubble separation methods is sometimes contracted to adsubble methods [1,8].

In order to acquaint interested graduate

students with this somewhat unusual group of separation techniques, some years ago the writer established an elective graduate lecture course on the subject. It runs for an academic quarter and is offered in approximately alternate years. It was originally offered for only 2 credits, but it recently has been expanded to 3 credits and has been opened to qualified seniors as well as to graduate students.

The text for the course is "Adsorptive Bubble Separation Techniques" by Lemlich [9]. Emphasis is placed on the first eight chapters which constitute half the book. Supplementary material, which includes some solved illustrative problems [10,11], is drawn from other sources. Table 1 presents an abbreviated outline of the course.

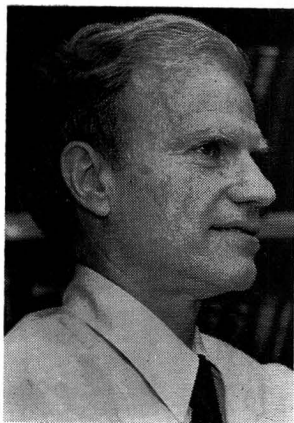
The course begins with an introductory overview of the field. The various adsubble techniques are briefly described and compared. The pervading importance of surface activity and solute surface excess are carefully noted.

SURFACES AND BUBBLES

NEXT, SURFACE TENSION is discussed and the common methods for measuring it are reviewed [12]. The equation of Laplace and Young for the pressure difference across a curved interface is derived, and the result is applied to the submerged bubble, the free bubble, and the Plateau border. For reinforcement of learning, these three special cases are also derived directly from fundamental force balances.

TABLE 1
Abbreviated Outline of Course

1. Introduction
2. Surfaces and bubbles
3. Foam
4. Adsorption
5. Foam fractionation
6. Flotation
7. Foamless separations
8. Student presentations



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The generation of bubbles is described. Empirical [13] and theoretical [14,15] unimodal frequency-distribution functions are discussed, as well as pathological [bimodal] distributions [16]. Mean bubble radii based on various combinations of moments are introduced. The propriety of $r_{3,2}$ for adsorption and $r_{3,1}$ for drainage is derived.

The general morphology and characteristics of foam are presented [17,18]. Foam stability is explained in terms of the liquid and surface viscosities, the Gibbs and Marangoni effects, and, for ionic surfactants, the electrostatic repulsion across the film. The two general mechanisms of foam instability are delineated, namely film rupture [19] and interbubble gas diffusion [13]. Theory for the latter mechanism [13] as well as for foam drainage [16,20-22] is covered in some detail.

Various methods for measuring pertinent properties of and in foam are presented. These include surface viscosity by movement within films [23], film thickness by diffraction of light [23], and liquid content of foam by total collapse or by electrical conductivity in situ [24,25]. Bubble sizes are usually measured photographically. Accordingly, derivations are presented in detail for the correction to the frequency size distribution for planar statistical bias [13] and its step effect [26] on any mean radius [true $r_{j,k}$ = planar $r_{j-1,k-1}$].

The general Gibbs adsorption equation [27] is detailed and several important special cases are

discussed. For the sake of clarity and reinforcement, the simple case of a pure dilute solution of a simple nonionic surfactant is also derived directly [28].

The Langmuir isotherm [29] is derived and its important limiting cases are noted. The effects of insufficient collector, excess collector, micelles, and competing ions are considered. Selectivity is discussed.

SEPARATION METHODS

THE SIMPLE, STRIPPING, enriching, and combined modes of operation are presented in detail. The important concept of effective concentration in the upflow is introduced. Transfer units and theoretical stages are discussed and methods for their calculation are derived [10,30,31].

For utility as well as learning reinforcement, the limiting equations for separation in tall counterflow columns are derived from transfer units, theoretical stages, and also directly from fundamentals. The effect of internal reflux induced by coalescence in the rising foam is discussed [30].

The physical and chemical parameters affecting ion flotation are covered. The selectivity, thermodynamics, and kinetics of the separation are discussed.

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separation methods involve
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Precipitate flotation of the first kind, in which a separate surface-active collector is added to coat and thus float the precipitate, is distinguished from precipitate flotation of the second kind in which no separate collector is required. The effects of the various parameters are discussed and precipitate flotation is compared with ion flotation.

The elements of mineral flotation are presented. Some of the technology [32] is also surveyed. However, since mineral flotation belongs more properly in the field of mining engineering and extractive metallurgy, it is not covered in detail in this course which is intended primarily for students in chemical engineering.

The lumped parametric approach to analyzing

batchwise bubble fractionation is presented [33], and results are compared with experiment [34]. The theory is extended to continuous flow and also compared with the distributed parametric approach [35].

Solvent sublation is introduced and compared with bubble fractionation. It is also compared with conventional liquid extraction. The immiscible layer of solvent sublation can trap more than can the layer in liquid extraction which is limited by considerations of bulk equilibrium.

PRESENTATIONS AND DEMONSTRATIONS

SOME OF THE MANY systems separated by the adsubble techniques are surveyed throughout the course. Each student is then required to write a term paper and in some cases present a brief oral report on some group or aspect of these separations. Appropriate supplementary literature is provided.

Some typical topics are as follows: a) Applications to sewage treatment; b) Phenol removal; c) Natural adsubble phenomena in the sea and the

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effect on the marine aerosol; d) The adsorptive droplet separation methods (which are the liquid-liquid analogs of the adsorptive bubble separation methods).

It has been the author's experience that the inclusion of an occasional, simple, inexpensive but well-chosen brief demonstration can add spice to a lecture course while at the same time illustrate principles in a convincing manner and thus enhance the learning process [36,37]. Some examples for this course include the following: (a) A razor blade floated by surface tension and dramatically pushed aside by a single tiny droplet of surfactant but scarcely moved by a second droplet; (b) The foam fractionation of dilute crystal violet chloride from scarlet red in the presence of sodium sulfate and the collector sodium lauryl sulfate by simple shaking (and the failure to visibly separate in the presence of too much collector); (c) The bubble fractionation of dilute crystal violet chloride in the presence of sodium sulfate in a

tall narrow vertical glass tube by bubbling with air or nitrogen; and (d) the simple Crits ring test for the presence of trace surfactants in water [38] that has been shown to function by virtue of transient adsubble separation [39].

CONCLUDING REMARKS

BY THE END of this course the student has become familiar not only with the adsubble techniques but also with some of the important universal concepts of surface phenomena. He has also learned some ways in which they can be applied. He is thus better equipped to deal with a class of problems that might otherwise cause him great difficulty during his subsequent professional career. □

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Continued on page 186.

offered on a yearly basis and has enrollments of 12 to 15 students of which 30% have been of graduate standing. Larger enrollments have been handled by giving the laboratory twice a year. This approach has allowed for more individualized instruction which is quite necessary in a laboratory of this type since the equipment is generally expensive and chemicals are somewhat toxic.

The course is developed to achieve a balance of many of the disciplines of polymer science and technology. This necessitates a survey approach. However, homework problems are specific enough for the student to obtain a deeper insight into many of the topics covered in the lecture.

The course is divided into three one credit sections for flexibility. A list of the required experiments is given in Table 2.

TABLE 2. Laboratory Experiments

- I. POLYMERIZATION (1 credit)
 1. Suspension Polymerization of Polystyrene
 2. Preparation of Phenol-Formaldehyde and Phenol-Resorcinol Resins
 3. Preparation of Polyurethane Foams
 4. Kinetics of Polyesterification
 5. Preparation of Polysiloxane Elastomer
- II. CHARACTERIZATION (1 credit)
 1. Infrared Analysis of Polymers
 2. Fractionation of Polystyrene and Molecular Weight Measurements by Solution Viscosity
 3. Flammability of Polymers
 4. Differential Scanning Calorimetry of Polymers
 5. Nuclear Magnetic Characterization of Polymers
- III. FABRICATION AND TENSILE TESTING (1 credit)
 1. Molding of Phenolic Laminates and Composites
 2. Tensile Testing of Rigid, Thermoplastic, and Elastomeric Polymers
 3. Compression and Injection Molding of Thermoplastics and Thermosets
 4. Extrusion of Thermoplastics (Polypropylene)

The text used for the laboratory is, *Laboratory Preparation for Macromolecular Chemistry*, E. L. McCaffery, McGraw-Hill (1970).

Before the students can begin each experiment they must hand in a short report on the toxicity and carcinogenic properties of each chemical (including common solvents) which is used in the experiment. I might add this single requirement has produced desirable, positive effects on laboratory techniques. The students work in squads of

two or three since most of the experiments are elaborate enough to be difficult for one person either to control or set up. It normally takes three hours for completion of most of the experiments, however certain long experiments are split into two laboratory periods. The polymerization reactions which unfortunately cannot be split can take long times, especially the pearl polymerization of styrene. Some undaunted students have been known to stay ten hours to complete that experiment after two initial failures!

Additional experiments on light scattering, adhesion and fracture, and copolymerization have been designed and will be included in the following year.

These introductory courses have been useful for many graduate students embarking on higher level courses specific to polymers and particularly useful for the undergraduate ChE student who wishes a background of polymers to round out his academic career. Although the department does not yet require such a course for undergraduates, a large majority of our students avail themselves of the opportunity. □

LEMLICH: Adsuble Methods

Continued from page 182.

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