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COMMUNICATION

Adsorptive Bubble Separation Methods

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Summary

All techniques that may be classified at present as "adsorptive bubble separation methods" are described; their relationship to one another is displayed in a schematic diagram which is based on a previous publication.

INTRODUCTION

An attempt has been made to overcome the confusion which exists regarding the interrelationship of a group of techniques, known collectively as adsorptive bubble separation methods (1). These methods have been defined as any in which separations are accomplished by the adsorption of material on bubbles, and have been classified on the basis of whether or not a foam is required for the separation. Although the scheme has proved useful, it is incomplete and in need of rearrangement. In the present note, the mechanisms of the methods as they are currently understood, and their interrelationship, will be presented. Most of the references are to publications in which the techniques were first described.

DISCUSSION

The separation achieved by adsorptive bubble methods takes place predominantly at the gas-liquid interface of bubbles, while the latter are in the bulk of the aqueous solution. It appears more reasonable therefore, that the methods be classified according to the mechanism

of this adsorptive process, rather than on the basis of whether or not a foam is formed. It is suggested that the methods be divided according to whether flotation occurs of particles on the one hand, or of ions and molecules on the other. Hitherto the term *flotation* has been used only for the removal of *particulate* material but this is inconsistent with the definition of the word (2), which imposes no such restriction. To make a distinction, however, between the flotation of particles and that of ions or molecules, the terms particulate flotation and colligend flotation are proposed, respectively. The term *colligend* was introduced in the description of ion flotation (3, 4) and refers to ionic or molecular species "which is about to be collected." One of the techniques to be described, namely ion flotation, can occur by either particulate or colligend flotation, and cognizance of this is taken in the schematic representation shown in Fig. 1. A description of each method follows.

Ion flotation (3, 4) involves the removal from a dilute solution of a surface-inactive ion (colligend) by the addition of a surfactant (collector). The flotation of these entities results in the formation of a foam in which a solid phase is deposited. The collector is usually an ion the charge of which is opposite to that of the colligend, but it may also be a long-chain amine which forms surface-active complex ions, e.g., $\text{Cu}(\text{NH}_2\text{R})_4^{2+}$. If the concentrations of collector and colligend are relatively high, a precipitate is formed which is subsequently removed by particulate flotation; under these conditions ion flotation is a form of precipitate flotation. At lower concentrations, no precipitate is formed prior to the advent of gas but instead, collector adsorbs on the bubbles and holds the colligend to it. When the bubbles reach the surface of the solution, the precipitate is deposited in the foam.

If, prior to flotation, a small amount of an immiscible liquid is spread on the surface of the solution, no foam forms and sublate is retained in the layer either as a solution or a suspension. This method, which is known as *solvent sublation* (4), is not an adsorptive bubble separation technique but merely a means of collecting floated material. Although it was first used as an adjunct to ion flotation for convenient removal of sublate salts (3), it is applicable to other adsorptive bubble separation methods. For example, a modification of this procedure, known as extractive solvent sublation (5), has been used for collecting floated precipitates.

Foam fractionation. In this technique, surface-active material is removed by flotation to form a foam which contains no solid phase. Enrichment of one species over another occurs both on the bubbles

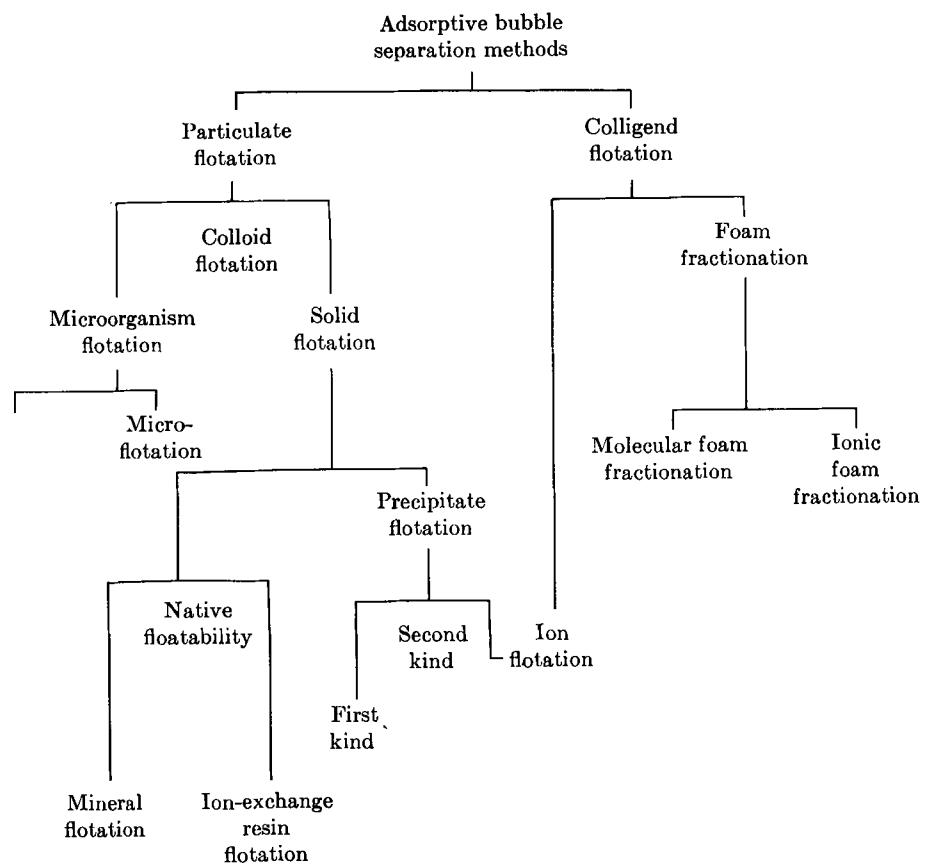


FIG. 1.

while in solution, and in the lamellae of the foam. The colligands may either be surface-active molecules (6), in which case the process might be called *molecular foam fractionation*, or surface-inactive ions which can be removed using oppositely-charged collectors (7). The latter method, which is similar to one form of ion flotation except that no insoluble product occurs in the foam, might be called *ionic foam fractionation*.

Techniques involving particulate flotation may be subdivided according to whether microorganisms, colloids, or solids are floated.

Microorganism flotation involves the removal of microbes, such as bacteria and algae, by flotation (8).

Microflotation (9) is a technique within this field in which the microorganisms are first coagulated and then floated at low flow-rates with collectors of low solubility.

Colloid flotation (10, 11) at present involves the removal of hydrophobic colloids only. Flotation is achieved by adding a collector ion of a charge opposite to that adsorbed on the particles. The latter become coated with the surfactant, and float to form a foam in which the coagulated colloid is deposited.

Mineral flotation was probably first used by the ancient Greeks, and requires little introduction (12, 13). Solids which are not naturally floatable are made to float by adsorption on their surfaces of hydrocarbon-bearing ions or molecules.

Native floatability. It is well known that some solids float without the aid of added substances. This property may arise if, on cleaving the solid, at least some surfaces form without the rupture of interatomic bonds, other than residual bonds (14). Included in this class are many solids which form molecular or inorganic sheet crystals, or are organic salts, hydrogen-bonded compounds, or substances containing zwitterions.

Ion-exchange resin flotation (15). Cation- and anion-exchange resins have been floated using cationic and anionic surfactants, respectively. The collector ions are held by electrical attraction to the charged sites on the resins; in this way the particles acquire a hydrophobic surface and can be floated.

Precipitate flotation includes all processes in which an ionic species is concentrated from an aqueous solution by forming a precipitate which is subsequently removed by flotation. Besides one form of ion flotation in which the ion is precipitated by a surfactant, the field

includes two other methods, known as precipitate flotation of the first and second kinds.

Precipitate flotation of the first kind involves the flotation of precipitate particles by a surface-active species; the latter is not a chemical constituent of the precipitated substance and occurs only on the surface of the particles (16, 17, 4).*

Precipitate flotation of the second kind. Precipitates may be floated without using a surfactant because it is possible to form a solid that has a hydrophobic surface, by the mutual precipitation of two hydrophilic ions (18).

CONCLUSION

The scheme above has been introduced because (a) a need exists for a complete list of adsorptive bubble separation techniques, and (b) sufficient is probably known about their mechanisms to allow of a more useful classification than that given originally. Among the features of the present scheme which are open to conjecture are (a) the flotation of microorganisms has been treated separately, rather than as a branch of colloid flotation, because living matter is being removed; (b) other than that of microflotation, no suggestion has been made for the subdivision of microorganism flotation; and (c) techniques which differ from the above processes only in what they aim to achieve have been omitted. For example, colloids are able to stabilize foams and to adsorb ions on their surfaces. The addition of a colloid, and its subsequent flotation, therefore enhances the removal of surfactants and ions from solutions of each, respectively. In both cases the process occurring is colloid flotation, and subdivisions to account for such minor variations seem unwarranted.

The original nomenclature scheme (1) was unsatisfactory because of the omission of known techniques and the inclusion of others which have either not yet been discovered or are not adsorptive bubble separation methods at all. For example, no case of *molecular flotation* is known while *bubble fractionation* and *solvent sublation* are merely techniques for the collection of material which has been floated by one method or another. In addition, there are inconsistencies in the original classification. For example, the flotation of ores and precip-

* First references to this method were made independently by Voznesenskii et al., Skrylev and Mokrushin, and by Baarson and Jonaitis. The latter acted on a private communication from F. Sebba.

itates should have been subdivisions of macroflotation, and adsorbing colloid flotation a branch of microflotation, according to the definitions given. Instead, all five methods are considered as subdivisions of the same group. Further, the classification of ion flotation unfortunately implies that this method can only occur by a froth flotation mechanism. Also confusing is the definition of microflotation which is different from that given originally and used since the publication of the scheme.

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