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A New Type of Adsubble Methods: Booster Bubble Fractionation—Hastened and Improved Bubble Fractionation of Low-Foaming* Solutions

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Summary

The enrichment of very dilute surface-active substances when air or nitrogen bubble through the solution is known as bubble fractionation. The addition of vapors of certain organic liquids has led to an improved and accelerated separation method called booster bubble fractionation (BBF). For the fractionation of dyes in a test apparatus, pentane and chloroform appeared as excellent boosters while ethyl ether and ethyl acetate had no effect. Diagrams showing several foam heights and a periodically changed surface-active Patent Blue content in the bulk demonstrated that water and organic solvents form layers which are only stable in the presence of the surface-active compounds. The gas cycle saturator/fractionator/top-fraction-receiver was operated by a peristaltic pump, the liquid passing by gravity. In a continuous separation process of both 10 ppm and 1 ppm Patent Blue/Neucoccin solutions at 10 liters/hr (=25 × fractionator volume), PB was concentrated by a factor of 10 in the top fraction and nearly totally recovered. Säuregrün, which shows no shift in foam fractionation, could be enriched by a factor of 7 by BBF. The volatility and low solubility of the boosters offer fractions with negligible reagent pollution. Because of a possible specific relationship between boosters and surface-active substances, bubble chromatography with selected organic vapors is suggested.

In 1965 Dorman and Lemlich (*1*) pointed out that low concentrations of surface-active compounds can be enriched by passing gas

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* *Note added in proof: Non*foaming Patent Blue/Neucoccin solution (down to 1.0 and 0.01 ppb) can now be fractionated by booster bubble fractionation ("Kugelschaum-Chromatographie," K. Maas, *Fette, Seifen, Anstrichm.*, in press).

bubbles through their solution. This separation method was named bubble fractionation. Since 1966 Karger et al. have published about successful experiments in the field of solvent sublation (*2,3*), which was suggested by Sebba in 1962 (*4*). In this technique the aqueous solution with ascending nitrogen bubbles is covered with an immiscible organic solvent—usually octanol or anisol—in order to dissolve the substances adsorbed at the bubble interface or to deposit the compounds at the interface between the two liquids. Both methods are classified as nonfoaming bubble separation in the system of adsorptive bubble separation established in 1967 (*5*). The present publication shows a connecting link between booster bubble fractionation and the other types of foam separation methods, especially bubble fractionation, solvent sublation, foam fractionation, and—with suspensions—flotation. This is in accord with Lemlich's remark that ". . . it is not unreasonable to expect that new terms of new adsubble methods will appear in the future" (*6*).

PHENOMENOLOGY

Usually nitrogen or air is pressed through an orifice or fritted filter in foam fractionation; often the gas is moistened by means of a saturator. In laminae column foaming it has been shown that this preconditioning of the gaseous phase can be eliminated by recycling with a water blower or a electromagnetic membrane pump (*7*). Another recycling aid is a peristaltic pump, drawn as A in Fig. 4.

At low concentrations of the surface-active substances foam fractionation becomes bubble fractionation with much lower enrichment and stripping effects. However, filling the saturator with certain volatile organic liquids leads to fast and exact separation through an increased generation of foam. It is of interest that increasing the foam height by the air/vapor mixture affects only surface-active substances. This effect is reminiscent of the action of boosters in fuses and so this method was named booster bubble fractionation.

The phenomenology shall be described by studying the behavior of the testing apparatus shown in Fig. 1 (recycling peristaltic pump and saturator not drawn, see Fig. 4).

The testing apparatus shows several properties which are disadvantageous in bubble fractionation. It works with a very coarse fritted filter (Schott G1), with low liquid levels (e.g., 5, 10, 20 cm), with a relatively large diameter (6 cm), and with gas throughput rates of between 25 and 700 liters/hr. A concentration gradient in the liquid is impossible because of the intense turbulence of the coarse

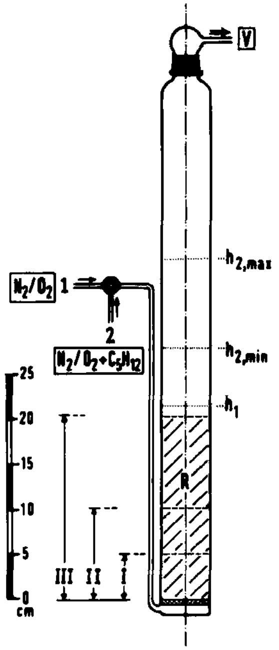


FIG. 1. Testing apparatus for booster bubble fractionation.

bubbles. The best proof(test) would be to change the air/vapor mixture and use pure air. The separation obtained is destroyed in a few seconds with reversion to the starting solution.

The characteristic foam heights reached during the test series are indicated by dotted lines. h_1 is the height with pure air (1), the bubbles coalescing immediately after the gas stream is stopped. By passing the air/vapor mixture (2) through the liquid first a maximum foam height $h_{2,\max}$ is reached which decreases in time to $h_{2,\min}$. Figure 2 gives a comparison between the maximum foam heights with and without booster and with and without surface-active Patent Blue at several throughput rates of the gaseous phase.

Pentane affects the foam height of a surface-inactive Neucoccin solution only slightly, but a Patent Blue solution is affected strongly. As Fig. 3 shows, at low gas rates a periodic exchange of the surface-active substance between foam and liquid phase (residue R) is obtained through a periodic increase and decrease of the foam height. The system Patent Blue/Neucoccin is an ideal one because it is possible to determine the concentration of PB in the red NC-solution (exactly 1% at low contents, ca. 5% at a ratio of 1:1). Since Neucoccin remains

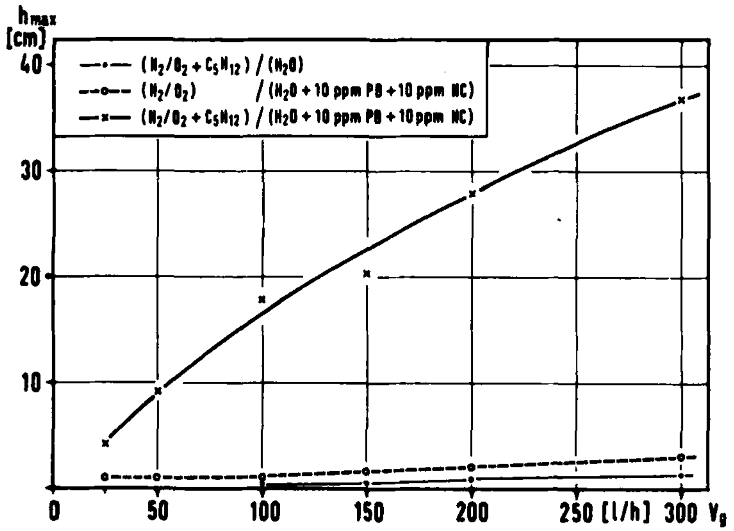


FIG. 2. Foam height h_{max} as a function of gas throughput V_g, gaseous phase and liquid phase.

in the residue R, one can follow the rapid decrease of the PB concentration in the bulk.

The enrichment in the foam can only be determined by spectrometry. For the accurate fractionation in the continuous separation process see below.

An indication of the value of BBF (booster bubble fractionation) is the enrichment of Säuregrün (a triphenylmethane dye). Ostwald and Siehr showed (*8,9*) that the compositions of the foam fraction and the residue of this compound have no detectable difference. They conclude that in this case the foaming is more an effect of the orientation of the molecules than of the adsorption at the surface, according to Gibbs. However, even Säuregrün can be concentrated by BBF (see Fig. 6)!

The test apparatus can be used for batchwise separation when a vessel in the recycling gas system removes the sucked-off foam. Advantageously, the BBF-foam has no stability without bubbling of the air/vapor mixture, so the top fraction assumes only the real liquid volume. Based on the surface-active substance content, and hence on the foam height, the liquid level must be so positioned that the enriched foam just reaches the top of the tube. With an input device below the liquid level and an output device near the fritted filter this apparatus can also be used for continuous fractionation.

TECHNIQUE AND RESULTS

The arrangement for BBF can be likened to a simple washing-flasks apparatus (Fig. 4); all parts are commercially available or only somewhat modified. The short flask type D instead of tubings was chosen intentionally in contrast to other adsubble methods; the saturator B is also a general type (Fig. 1).

In principle two flow systems appear.

1. The closed gas/vapor recycling system is operated by the two-armed (better three-armed) peristaltic pump A. Compressed air or nitrogen bubbles through the saturator, a coarse fritted filter washing-flask filled with pentane or some other suitable organic liquids. The saturated gas bubbles through the fractionation-flask D with the feed solution, passes through the top-fraction receiver G, and returns to A.

2. The liquid runthrough is operated partly by gravity, partly by the recycling system. The starting solution is fed from the reservior E, passes D, and the bottom-fraction flows to the container F by siphon-action. The enriched foaming top-fraction is sucked into G by the gas cycle.

The continuous operation is begun by having the peristaltic pump slowly revolving and the airing stopcock (1) open. The volatile liquid is drained from C into the saturator B up to a height of 1 to 3 cm.

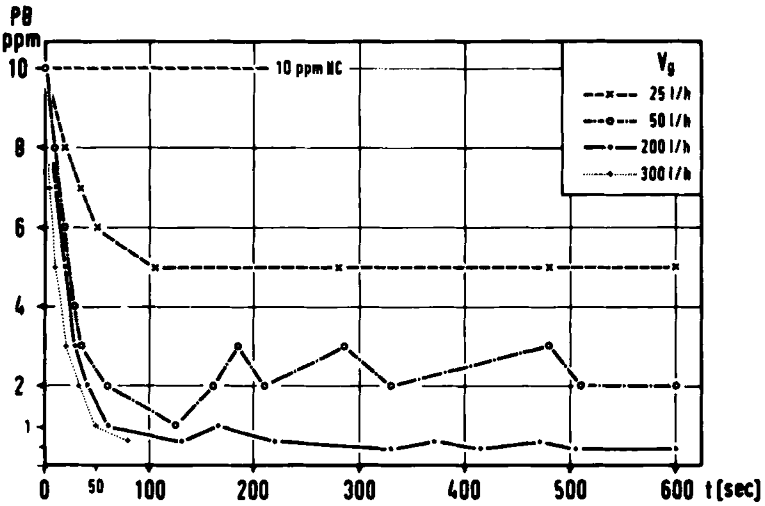


FIG. 3. Removal of PB from a solution of each 10 ppm Patent Blue and Neucoccin at several gas rates V_g (rest in the liquid).

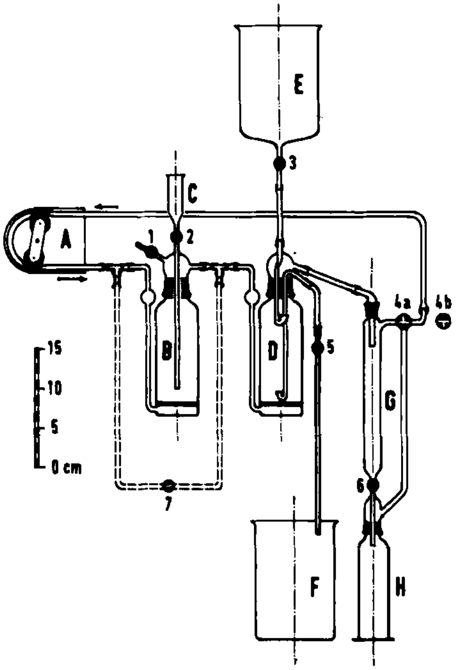
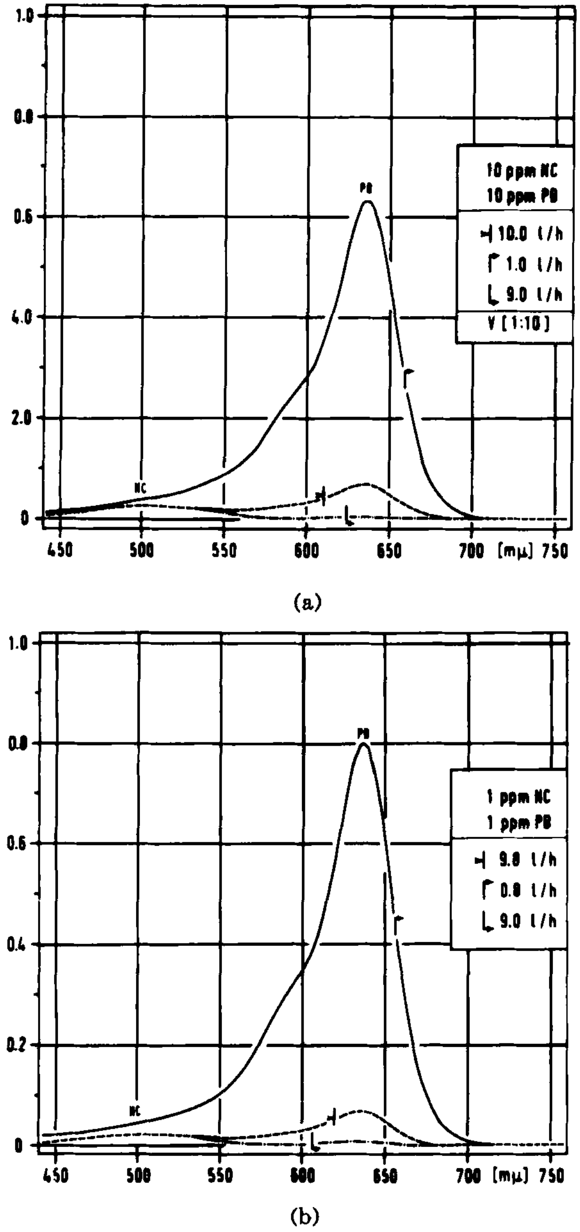


FIG. 4. Flask-type apparatus for the continuous booster bubble fractionation. (A) Peristaltic pump; (B) saturator; (C) booster-liquid reservoir; (D) fractionator; (E) starting solution reservoir; (F) bottom fraction container; (G), (H) top fraction receiving device.

The starting solution is fed from E to D, and stopcock (1) (preferably a needle-valve) is closed in order to overcome $h_{2,\max}$; well-foaming systems require slow filling of D to enrich the surface-active substance in the foam during this time. By increasing the gas rate the minimum foam height $h_{2,\min}$ reaches the overflow to G. Stopcock (5) of the solution-filled siphon is adjusted to the wanted residue level of bottom-fraction in F. The closed recycle system holds the liquid level in D constant for a long time; it can be regulated by short openings of (1). The foam flows to the calibrated vessel G and breaks down immediately; it is often a clear liquid which drops into G. The top-fraction is withdrawn during the separation process by bringing the three-way stopcock from position 4a into 4b and opening (6). The system provides for changing the vapor concentration [bypass line with stopcock (7)].

Figure 5 demonstrates the fractionation effect at throughput rates



(a)

(b)

FIG. 5. Fractionation analysis of BBF by spectrometry; $V_g = 400$ liter/hr. (a) 10 ppm PB, 10 ppm NC (samples diluted for measurement 1:10). (b) 1 ppm PB, 1 ppm NC (samples directly measured; $d = 1$ cm).

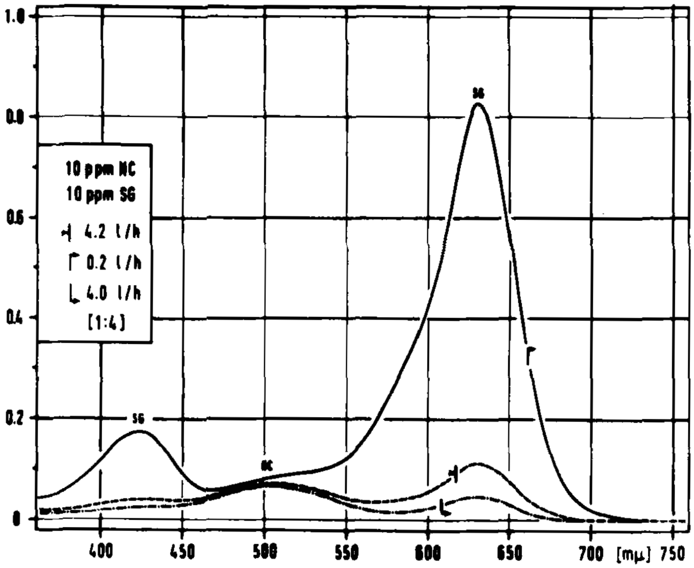


FIG. 6. Fractionation of Säuregrün and Neucoccin (each 10 ppm); $V_g = 400$ liter/hr; samples diluted for measurement 1:4, $d = 1$ cm.

of 10 liters/hr (30 times liquid volume in D) with each 10 ppm (5a) and 1 ppm (5b) of PB and NC (note a second absorption maximum of PB near 420 mμ).

Experiments were also carried out with such other dyes as Titangelb, Gentianaviolett, and Brillantgrün. Acid and basic dyes were studied separately to avoid molecular-flotationlike effects.

Laminae column foaming (7) confirmed the results of Ostwald and Siehr (see above) that though the solution foams, no separation can be obtained. In contrast, Fig. 6 shows the remarkable BBF fractionation. To solve the separation problem as well as the enrichment problem, a solution of 10 ppm Säuregrün (SG) and 10 ppm NC was used.

A great advantage of the new method is the volatility of the booster. In addition to low solubility, it offers small reagent costs and negligible pollution of the bottom and top fractions by extraneous substances.

Investigations with ca. 40 organic and inorganic gases and liquids at 15–20°C showed the interesting result that pentane and chloroform, for example, give excellent separations, while diethyl ether and ethyl acetate have no—or nearly no—effect. Booster action is probably based on the formation of water/organic solvent layers which are stabilized by the surface-active substances; cf. periodic fractionation in Fig. 3. Systems similar to these were produced by Manegold (*11*) and De Vries (*12*) by shaking mixtures of water, organic solvents, and detergents. Other organic molecules, such as ketones, quinones, acids, and bases, are presently being studied. A possible relation between specific vapors in the gas cycle and certain surface-active compounds in the solution would lead to real bubble chromatography with selected boosters.

Acknowledgments

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