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Studies in Solvent Sublation: Extraction of Methyl Orange and Rhodamine B[*]

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Summary

The technique of solvent sublation has been investigated for the solutes methyl orange and rhodamine B together with the cationic surfactant, hexadecyltrimethylammonium bromide. In solvent sublation, gas bubbles generated in an aqueous phase are used to selectively extract material into a nonaqueous phase, which is immiscible with the water. Presumably attachment to the bubbles occurs through adsorption at the gas-liquid interfaces by surface-active species. The effects of parameters such as gas flow rate and concentration of surfactant on the rates of extraction of the two dyes have been investigated. Marked differences in the behavior of the dyes have been found, suggesting different mechanisms of extraction. A direct comparison has also been made between solvent sublation and solvent extraction, the latter using vigorous shaking to provide intimate contact between the liquid-liquid interfaces. Finally, the potential of solvent sublation in the separation field has been discussed.

Although selective adsorption at gas-solid and liquid-solid interfaces has been extensively employed in separation techniques, considerably less attention has been paid to the use of selective adsorption at gas-liquid interfaces for separation. Recently, however,

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a series of techniques using gas bubbles and foams for selective adsorption has been under close study by several workers. Such techniques as foam fractionation (*1*), ion flotation (2), colloidal fractionation (3), and solvent sublation (*4*) have been investigated for possible uses in the separation field.

In this paper, we would like to describe some studies we have recently made on the technique of solvent sublation. Solvent sublation was originally introduced by Sebba (*4*), as an auxilliary method to ion flotation when persistent foams occurred. In this method, two immiscible phases are used—usually water and a less dense organic phase which is placed above the water in the extraction column. At the start of a run the sample to be separated is in the aqueous phase. The sample will usually contain ionic solutes along with a charged surfactant. Gas is bubbled through the aqueous phase and thence into the nonaqueous phase. Presumably the surfactant will adsorb on the gas-liquid interfaces as the bubble travels through the aqueous phase. If this agent is oppositely charged to the solute in the water, then a solute-surfactant ion pair may form at the gas-liquid interface, with its subsequent extraction into the nonaqueous phase. It is also possible that the surfactant may complex with the solute at the interface, perhaps through some type of chelation. Alternatively, a solute-surfactant ion pair or complex may form in solution and be subsequently adsorbed on the bubble surface. Also surface active agents themselves may be extracted into the nonaqueous phase. There are thus several different processes by which extraction from the aqueous to the nonaqueous phase may occur in solvent sublation.

We have selected for study two dyes, methyl orange (MO) and rhodamine B (RB), because of the ease of their analyses and the ability to follow the extraction process while in progress. Also in basic media MO is anionic and RB is zwitterionic, so that their experimental behavior with the cationic surfactant, hexadecyltrimethylammonium bromide (HDT), might be expected to be different. Various parameter studies using MO, RB, and HDT will be described. These studies will be of aid in elucidating the mechanism of extraction for RB and MO and thus also in understanding the general sublation process.

At first glance, because of the use of two immiscible phases, the sublation technique may seem somewhat similar to the more familiar solvent-extraction technique, in which vigorous shaking provides intimate contact between the two phases. However, the two methods are fundamentally different and experiments designed to show these differences will be described in this paper. Finally, we shall discuss the potentiality of solvent sublation in the separation field.

EXPERIMENTAL

Apparatus

The basic experimental setup is shown in Fig. 1. Nitrogen gas was first passed through a presaturator containing distilled water in order to prevent any spurious evaporation in the extraction column.

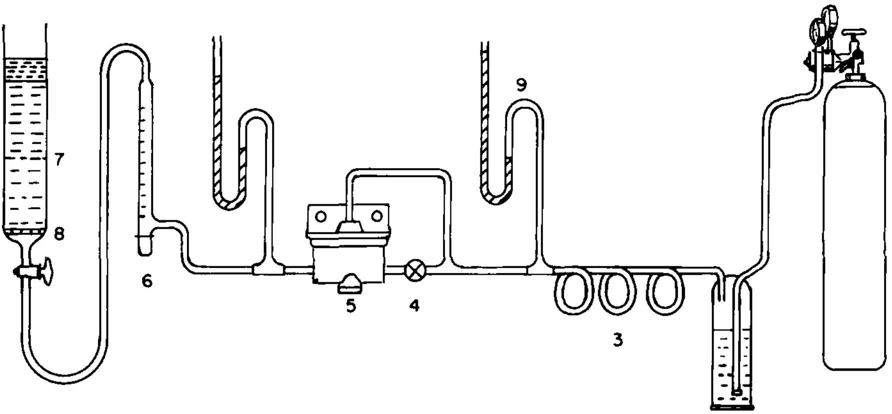


FIG. 1. Basic experimental apparatus for solvent sublation. 1, nitrogen tank; 2, Pyrex # 12-9055 gas washing bottle; 3, 2 ft of ¼-in. copper tubing packed with glass wool; 4, Nupro #B-4M fine metering valve; 5, Moore #63 BUL flow controller; 6, 10-ml soap-bubble flow meter; 7, extraction column, 463 × 45 mm; 8, 30-mm porous glass frit, Corning #39570-30M; 9, open-tube Hg manometers.

A 2-ft section of ¼-in. coiled copper tubing loosely packed with glass wool was placed next to the presaturator to trap out any excess water droplets. For constant-flow-rate control a Moore 63BUL low-flow controller with a Nupro fine metering valve was placed in the line. A soap-bubble flow meter and open-tube mercury manometer were used for flow-rate measurements, as shown in Fig. 1. From the flow meter, the gas traveled through a medium 30-mm porous glass frit and thence into the extraction column. In the flow system, all connections were made with ¼-in. copper tubing, except for the more flexible tygon tubing connection from the flow meter to the column. The open-tube manometer upstream from the Moore flow controller served as a constant pressure reference. With this setup relative deviations in flow rate were 1% using the medium frit and 5% using the coarse porous glass frit.

Reagents

The two dyes, methyl orange (MO) (Mallinckrodt Chemicals) and rhodamine B (RB) (Eastman Organic Chemicals), and the cationic surfactant, hexadecyltrimethylammonium bromide (HDT) (Matheson, Coleman, and Bell) were recrystallized from the following solvent systems, respectively: water, acetone-ether, and acetone-water. The solvent, 2-octanol (Eastman Organic Chemical) was doubly distilled for purification.

Procedure

Before use, both solvents were presaturated with one another to minimize solubility effects and subsequent changes in volume. Also, all solutions were freshly prepared daily to minimize any changes that might occur with time.

A 300-ml aqueous solution of the required concentration of dye at pH 10.5 (NaOH) was first pipetted into the extraction column. Unless otherwise indicated, the concentrations of the dyes were 10^{-5} *M*. Next a solution of 3×10^{-3} *M* HDT (except for the HDT concentration studies) was made up by dissolving the required amount HDT in boiling water.* Upon cooling, a 1-ml portion was pipetted into the extraction column to give a concentration of 10^{-5} *M* HDT. To this aqueous solution was slowly added 25 ml of 2-octanol. Nitrogen gas was then slowly generated into the solution at the required volumetric flow rate for the specified length of time.

* Sebba (*4*) has suggested that the surfactant be dissolved in hot ethanol to break up any micelles formed in the recrystallization process. Since ethanol is soluble in both water and 2-octanol, complications might arise in its use. Therefore, it is felt that dissolving the surfactant in hot water represented the best compromise for breaking up micelles and for complete solubility in the aqueous phase.

At the end of the run, portions of the aqueous and octanol phases were collected for analysis.

The actual gas volumetric flow rate in the column, as the gas rises through the solution, was calculated by

$$F = F_m \frac{760 - P_w}{760} \frac{P + 14.7}{14.9} \tag{1}$$

where F is the gas volumetric flow rate in the column, F_m the gas volumetric flow rate measured at the soap-bubble meter, P_w the saturated water-vapor pressure at room temperature (25°C), and P the pressure reading on the manometer downstream from the flow controller.

The first ratio in Eq. (1) simply corrects the soap-bubble meter reading for the water vapor pressure. The second ratio is based on the fact that the gas enters the frit under a certain pressure which gradually decreases to atmospheric pressure as the gas breaks through the octanol layer. In view of this pressure change, it is apparent that there is a corresponding increase in flow rate as the gas rises through the liquid. The pressure above the frit was calculated to be 15.1 psi; however, since the pressure changes as the bubbles rises through the liquid from 15.1 to 14.7 psi, the average pressure may be taken as 14.9 psi. The use of an average pressure is justified, since we are considering small pressure changes.

The aqueous phase was adjusted to pH 1.5 (L & N model 7664 pH meter) with concentrated HCl prior to absorbance measurements. Using a Beckman DU-2 spectrophotometer, both dyes were found to follow Beer's law at pH 1.5 and not to interfere with one another. The two wavelengths and extinction coefficients were 510 mμ: $\epsilon_{MO} = 4.50 \times 10^4$, $\epsilon_{RB} = 2.10 \times 10^4$, and 562 m$\mu$: $\epsilon_{MO} = 1.65 \times 10^4$, $\epsilon_{RB} = 9.45 \times 10^4$. Relative deviations were found to be 3% in the analysis of the aqueous phase. The RB absorbance in the octanol phase was found to be strongly affected by the presence of alkali and surfactant, in agreement with the results of Rametta and Sandell (5). However, RB shows virtually no absorbance at the MO peak (419 mμ, $\epsilon = 2.65 \times 10^4$), and hence MO was analyzed in the octanol phase. A relative deviation of 3% was found for the analysis of MO in the octanol phase. The RB concentration in octanol was based on the difference between the original amount of RB and that remaining in the aqueous phase after a run.

Liquid-Liquid Extraction

The liquid-liquid extraction experiments were carried out in 1-pint reagent bottles with the aid of a mechanical shaker for mixing. After shaking for a 1-hour period, the solutions were allowed to stand for 15 to 24 hours prior to sampling in order to break up the emulsion which formed. Samples of octanol and water were then analyzed in the usual manner. Surface tensions were measured with a Cenco Model 70535 Du Nuoy tensiometer.

RESULTS AND DISCUSSION

Previous Studies

In a preliminary communication (*6*), we reported several exploratory studies on solvent sublation, using MO and RB as solutes. For both dyes it was found that equilibrium was not established in over 4 hours of gas bubbling time. We, therefore, presented our results in terms of the extraction coefficient E, and the separation factor ϕ:

$$E = \frac{\text{conc. (octanol)}}{\text{conc. (water)}} \tag{2}$$

$$\phi = \frac{E_{\text{MO}}}{E_{\text{RB}}} \tag{3}$$

rather than the more familiar distribution coefficient K, and separation factor β, used in solvent extraction to emphasize that E and ϕ are time-dependent, whereas K and β are not.

It was found that the extraction behavior of MO differed markedly from that of RB. Without HDT, no MO could be extracted into octanol in a 3-hour period; however, substantial portions of MO were rapidly extracted when HDT was included in the solution. On the other hand, RB could be extracted without HDT; however, when HDT was added, a marked depression in the rate of extraction of the dye occurred.

A study was made of the change in E with time of gas flow for both dyes, and for purposes of clarity a portion of that data is shown in Fig. 2. It can be seen in this figure that MO is rapidly extracted at the start of gas flow followed by a slower rate of extraction at longer gas flow times. The extraction of RB is seen to be the reverse of MO,

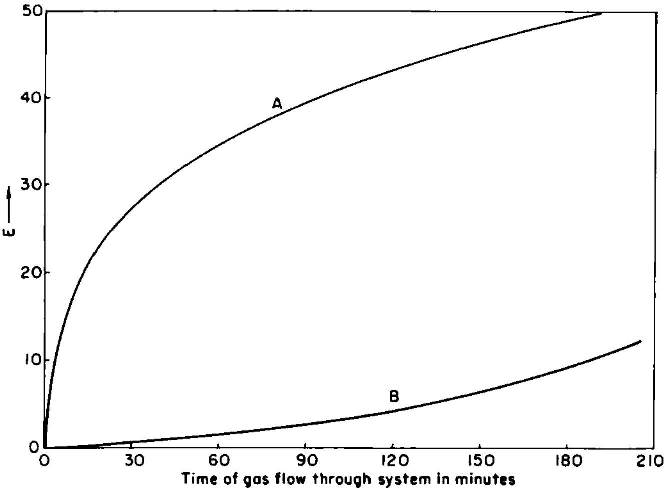


FIG. 2. Extraction coefficient as a function of time. Gas flow rate = 5 ml/min. A. 10^{-5} *M* MO, 10^{-5} *M* HDT, pH 10.5; B. 10^{-5} *M* RB, 10^{-5} *M* HDT, pH 10.5.

in that the rate of RB extraction increases with time. It was also found that the *E* values for the two dyes at any gas flow time were independent of whether the other dye was present.

As a result of the behavior illustrated in Fig. 2, a study was made of the separation of RB and MO by solvent sublation. It was found that for a sample of 10^{-5} *M* each of RB, MO, and HDT at pH 10.5, the separation factor ϕ was 510 in 5 min gas bubbling time and only 6.5 in 180 min gas bubbling time. Thus better separation of the two dyes occurred at shorter extraction times, a result opposite to the usual trend observed in liquid-liquid extraction. Also substantial amounts of MO were extracted in the short time periods.

All the data reported in our previous communication (*6*) suggested different mechanisms of extraction for MO and RB. Because MO is anionic in basic media and because the cationic surfactant was necessary to remove MO from the aqueous phase, it was postulated that the extraction of MO occurred through the formation of a surfactant-dye ion pair in the water. A peak shift for MO at pH 10.5 in the visible region of the spectrum was observed when HDT was added to the solution, indicating a strong HDT-MO interaction and thus giving further evidence of the formation of this ion pair. On the other hand, it was found that RB could be extracted into octanol without the use of surfactant, indicating that RB had sufficient surface activity to be preferentially adsorbed at the gas-liquid bubble interfaces. Because RB is zwitterionic at pH 10.5 and because no shift in the RB peak maximum in the visible region was observed on the addition of HDT, it was postulated that no surfactant-dye ion pair (or at the most only a very weak ion pair) formed between HDT and RB. Therefore, addition of HDT to an RB solution should depress the rate of extraction of RB through a competition between surfactant and dye for adsorption sites on the gas bubble surfaces in the aqueous phase. Experiments to be outlined in this paper shed further light on these mechanisms of extraction, and accordingly more will be said concerning these extraction processes in the following sections.

Effect of Gas Flow Rate on the Extraction of RB

It has been well established in foam fractionation (7) that the enrichment of solute in a foam decreases as the gas flow rate increases. This result is due to the increased entrapment of bulk liquid in the plateau borders between the foam bubbles. In solvent sublation, however, only gas-liquid interfaces, for the most part, are extracted across the water-octanol interface, and therefore, flow rate effects would be expected to be quite different in the sublation method relative to foam fractionation. (It is possible for a small amount of bulk aqueous phase to be "dragged" with the gas bubbles into the octanol.)

The effect of gas flow rate on the extraction of RB(10^{-5} M) with 10^{-5} M HDT at pH 10.5 is shown in Fig. 3. Flow rates of 5, 10, 20, and 30 ml/min were selected for study. It was difficult to maintain a constant flow rate below 5 ml/min, and agitation of the liquid-liquid interface was quite violent above 30 ml/min. These limits on gas flow rate, however, are not restricted to the sublation process but rather to the apparatus design. The use of a spinneret or capillary bubbler, instead of the porous glass frit, might alter the limits of flow rate quite markedly. Also the diameter of the extraction tube could play an important role in these limits.

In Fig. 3 it can be seen that for any given gas bubbling time, the E value of RB is larger the greater the gas flow rate (i.e., RB is extracted more rapidly as gas flow is increased). Presumably this

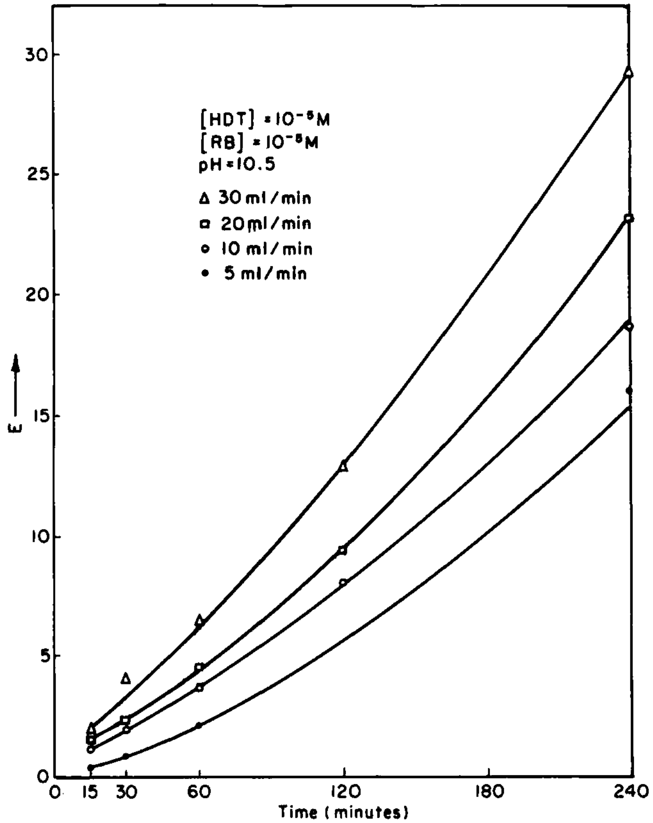


FIG. 3. Effect of gas flow rate on the rate of extraction of RB.

result is due to the fact that the larger the volume of gas generated in the aqueous phase in a given time period, the larger will be the total surface of the gas bubbles. Since RB is extracted into octanol by its own adsorption on gas bubble surfaces, the larger this surface the greater will be the *E* value.

Close examination of Fig. 3 further reveals that for any given gas flow rate, the rate of extraction of RB increases with gas bubbling time. This observation is readily understood in terms of the postulated extraction mechanism for RB. For any given gas flow rate, the longer the gas bubbling time the more surface that is generated in the aqueous phase, and consequently the more HDT that is extracted into the octanol phase. As the HDT concentration decreases in the aqueous phase, the surfactant cannot as effectively compete with RB for the adsorption sites at the gas-liquid interfaces, and accordingly the rate of extraction of RB increases.

No points below 15 minutes gas bubbling time are shown in Fig. 3 because of the inability to reproduce data in this region, especially at the high gas flow rates. There are several reasons for this lack of reproducibility at very short time. In the first place, the *E* values are quite small, so that slight errors in measuring the concentration of RB in the aqueous phase will be magnified in the *E* values. Second, it usually required 1 to 2 min to establish the correct flow rate in the column at the start of gas flow. The error in establishing the correct flow with the needle valve increased with increasing flow rate. Third, establishment of a stable liquid-liquid interface with reproducible bubble passage from the aqueous phase to the organic phase required approximately 5 min or more at the higher flow rates. Considerable bubble coalescence at the liquid-liquid interface occurred during this initial period. This third effect is probably related to a rapid change in interfacial tension between the two liquid phases during the first several minutes of a run. After 15 min of gas flow, all three effects had decreased to the point that reproducibility was as stated in the experimental section of this paper.

It is of interest to compare the *E* values for RB at different gas flow rates and times, such that the total gas volume generated in the aqueous phase remains constant. If the gas bubble diameter passing from the aqueous to the octanol phase is independent of flow rate and thus pressure drop across the glass frit, then the *E* values should be identical for the same volume of gas generated.

The results of this constant gas volume study are shown in Table 1. Examination of this table reveals that for a given volume of gas generated in the aqueous phase, the *E* values decrease markedly in going from 5 ml/min to 20 ml/min in gas flow rate. However, the *E* values are identical, within experimental error, for the 20 ml/min and 30 ml/min flow rates. These results strongly suggest that the bubble diameter crossing the liquid-liquid interface increases with flow rate to about 20 ml/min, where it remains fairly constant. In other words, low gas flow rates produce more efficient extractions of RB than high flow rates.

The diameter of the gas bubbles crossing the liquid-liquid interface is a result of two factors: (1) the bubble diameter in the aqueous

TABLE 1

Effect of Gas Flow Rate on the Extraction of RB at Constant Gas Volume (10^{-5} *M* RB, 10^{-5} *M* HDT, pH 10.5)

F, ml/min	Time, min	Vol., ml	*E*
5	60	300	2.1
10	30	300	1.9
20	15	300	1.6
5	120	600	5.6
10	60	600	3.7
20	30	600	2.4
30	20	600	2.4
5	180	900	10
10	90	900	5.7
20	45	900	3.4
30	30	900	3.5
5	240	1200	16
10	120	1200	8.0
20	60	1200	4.5
30	40	1200	4.4
10	180	1800	13
20	90	1800	6.8
30	60	1800	6.4

phase, and (2) the extent of bubble coalescence at the liquid-liquid interface prior to its passage into the nonaqueous phase (*4*). The results of Rubin et al. in their studies on ion flotation (*8*) lead us to believe that the bubble diameter in the aqueous should not vary too greatly with flow rate. We feel, therefore, that the marked changes in *E* for various flow rates in Table 1 are a result of the different extents of bubble coalescence at the liquid-liquid interface, with the higher flow rates producing more coalescence than the lower flow rates. Experiments designed to check these ideas are currently planned in our laboratory.

Effect of Gas Flow Rate on the Extraction of MO

The effect of gas flow rate on the solvent sublation of MO is shown in Fig. 4, initial concentrations being 10^{-5} *M* MO and 10^{-5} *M* HDT at pH 10.5. In this figure we have plotted the percentage of

MO extracted into the octanol phase vs. gas bubbling time rather than *E* vs. time, as in Fig. 3, for purposes of clarity. A comparison of Figs. 3 and 4 indicates that the effect of gas flow rate on the solvent sublation of the two dyes is quite different, as would be expected from the different mechanisms of extraction.

It can be seen in Fig. 4 that for any given gas flow rate, there is an initial rapid increase in the amount of MO extracted followed by a slow but definite increase in the percentage of MO extracted for longer time periods. This slow increase also appears to be flow-rate-dependent.

The initial rapid increase in the percentage of MO extracted is due to the extraction of the surfactant-dye ion pair into the octanol phase. Because the concentration of MO is so dilute (10^{-5} *M*), a substantial percentage of the MO is extracted in a very short time. It is difficult to ascertain from the experimental data whether this initial increase in the percentage of MO extracted is flow-rate-dependent, because of the lack of reproducibility of the data at gas bubbling times below 15 min, especially at the high flow rates.

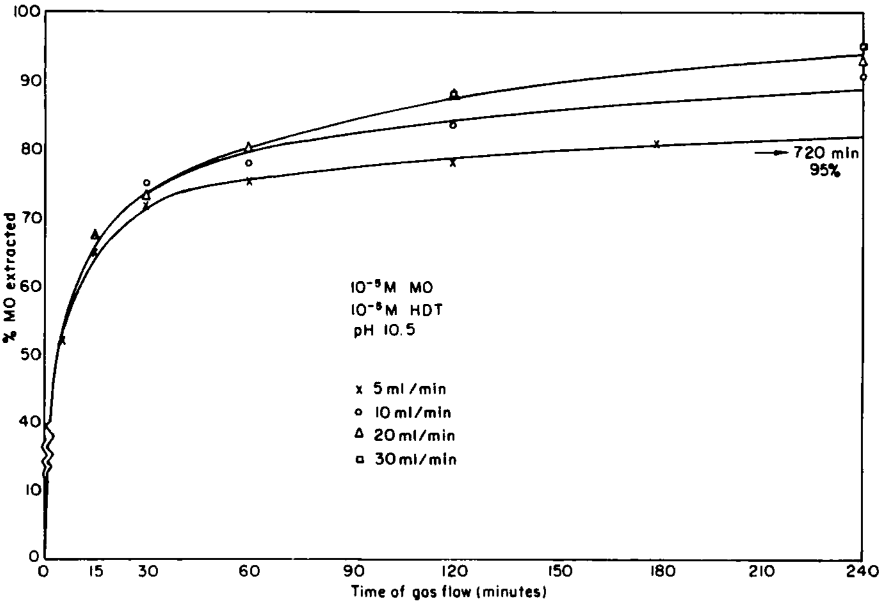


FIG. 4. Effect of gas flow rate on the rate of extraction of MO.

However, it is most reasonable to assume that the rate of extraction of the ion pair would depend on flow rate. The results of Rubin et al. (*8*) on the effect of gas flow rate (1.8 to 29.8 ml/min) on the ion flotation of copper(II) with sodium lauryl sulfate are in accord with this assumption. These authors found that at each flow rate a common limiting removal of copper was reached but that the rate of attainment of this limit was proportional to flow rate.

To observe this flow-rate effect in our solvent sublation system it would be necessary to increase the relative amount of surfactant-dye ion pair to the gas-liquid surface produced per unit time. This increase may be accomplished in two simple ways: (1) use a capillary bubbler, and (2) increase the concentration of both the surfactant and dye. Both procedures are currently being studied in our laboratory.

At long gas bubbling times, the results in Fig. 4 indicate a leveling off of the percentage of MO extracted into the octanol phase; however, there is still a slow but perceptible increase with time of the percentage of MO extracted. The rate of this increase seems to be greater the higher the flow rate. The leveling off below 100% removal in each of the curves of Fig. 4 is due to the low concentrations of surfactant-dye ion pair remaining in the aqueous phase. Indeed, Sebba (*4*) and Rubin et al. (*8*) have shown that complete removals of solutes require an excess of surfactant, whereas in our experiments the HDT concentration was equal to that of MO.

It is not entirely clear at the present time why the percentage of MO extracted continues to rise slowly in the long gas bubbling time periods. The causes are certainly tied up with the amount of gas-liquid interfacial surface extracted into octanol per unit time, since the rate of increase in the percentage of MO extracted is proportional to flow rate. The slow rate of increase may be due to the small amount of adsorption of the ion pair at the interface per unit time. The small concentration of ion pairs in the aqueous phase after long bubbling times, relative to the total surface produced per unit time, may result in only a small fractional coverage of each bubble. Since a smaller amount of ion pair would be on each bubble traveling across the liquid-liquid interface, the rate of increase in the percentage of MO extracted would be expected to be lower than at the initial time period, when the higher ion pair concentrations would allow a much greater portion of the surface of each bubble to be covered.

Effect of Surfactant Concentration on the Extraction of MO and RB

Since it had been previously established that the extractions of MO and RB were independent of one another, it was decided to examine the effect of surfactant concentration on the extraction of a sample of both dyes. Using 10^{-5} *M* RB, 10^{-5} *M* MO at pH 10.5 and varying concentrations of surfactant, the results are shown in Table 2. It is immediately clear from this table that the percentage of MO extracted into the octanol phase increases with increasing amounts of surfactant. On the other hand, 40% RB was extracted in 1 hour when no HDT was present; this percentage then decreased upon addition of surfactant until at an HDT concentration of 4×10^{-7} *M*, the percentage of RB extracted became independent of surfactant concentration. Indeed, roughly 20% RB was extracted using HDT concentrations which differed over two orders of magnitude. The trends observed for the two dyes individually were also reflected in the separation factor ϕ, which increased quite markedly as HDT concentration increased.

TABLE 2

Effect of HDT Concentration on the Separation of MO and RB[a]

HDT concn.	MO_{oct}, %	RB_{oct}, %	ϕ
None	0	40	0
1×10^{-7} *M*	1.0	38	0.02
2×10^{-7} *M*	1.8	36	0.03
3×10^{-7} *M*	2.8	30	0.07
4×10^{-7} *M*	3.4	21	0.10
5×10^{-7} *M*	4.0	20	0.17
1×10^{-6} *M*	8.2	19	0.38
5×10^{-6} *M*	43	19	3.1
8×10^{-6} *M*	65	21	6.7
1×10^{-5} *M*	75	19	17
2×10^{-5} *M*	97	19	190
5×10^{-5} *M*	99[b]	21	590

[a] Gas volumetric flow rate, 5.0 ml/min. Gas flow time, 60 min. 10^{-5} *M*, 10^{-5} *M* RB, with varying surfactant concentration at pH 10.5.

[b] Value based on aqueous-phase analysis and obtained by difference.

The behavior exhibited by RB in Table 2 can be explained in terms of the change in surface tension of the aqueous solution with

HDT concentration. In the first place, the surface tension of water saturated with octanol is quite low (ca. 37 dynes/cm^2 at 25°C). It is probable that addition of HDT to a solution of 10^{-5} *M* RB in water saturated with octanol will first decrease the surface tension. Apparently at an initial concentration of 4×10^{-4} *M* HDT, the surface tension becomes a constant during the greater part of the 60-min gas bubbling time, independent of the addition of more HDT. Measurement of the surface tension of these solutions with a Du Nuoy tensionmeter indicates a constant surface tension over a wide range of HDT concentrations above 5×10^{-7} *M*. With this instrument, however, it is difficult to pinpoint the exact HDT concentration at which the surface tension becomes constant. (It probably is somewhat lower than 4×10^{-7} *M*.) A more refined instrument is necessary to obtain this piece of data. (Indeed the solvent sublation of solutes such as RB may turn out to be an effective method for detecting small changes in surface tension.)

It is clear that the octanol used to saturate the water plays a prominent role in controlling the surface tension. The surface tension of the solution in turn controls the fraction of bubble coverage by RB and HDT, and when this surface tension becomes constant, the fractional bubble coverage of each species becomes constant, independent of the concentration of both components. Thus, given a constant gas flow rate and bubbling time, the % RB extracted into the octanol phase should be constant for initial HDT concentrations above 4×10^{-7} *M*.

Figure 5 presents data on the effect of HDT concentration on the rate of change of the extraction coefficient *E* with time. It can first be seen in this figure that the trend observed in Fig. 2 on the extraction of RB with 10^{-5} *M* HDT is again present; i.e., the rate of extraction of RB for any concentration of HDT increases with gas bubbling time; however, for the lowest HDT concentrations (10^{-7} *M* and 5×10^{-7} *M*) this rate of RB extraction becomes a constant value after long gas bubbling times.

In Fig. 5 the rate of RB extraction initially increases as the concentration of HDT decreases; however, these rates are only dependent on HDT concentration when the HDT concentration is below a certain value in the aqueous phase. For example, the *E* vs. time curve in Fig. 5 for an initial HDT concentration of 1×10^{-7} *M* is divergent from the other three curves at all points. On the other hand, the curves for HDT concentrations of 5×10^{-7} *M*, 10^{-6} *M*, and 5×10^{-6} *M* coincide at 15 and 30 min gas bubbling time. At 60

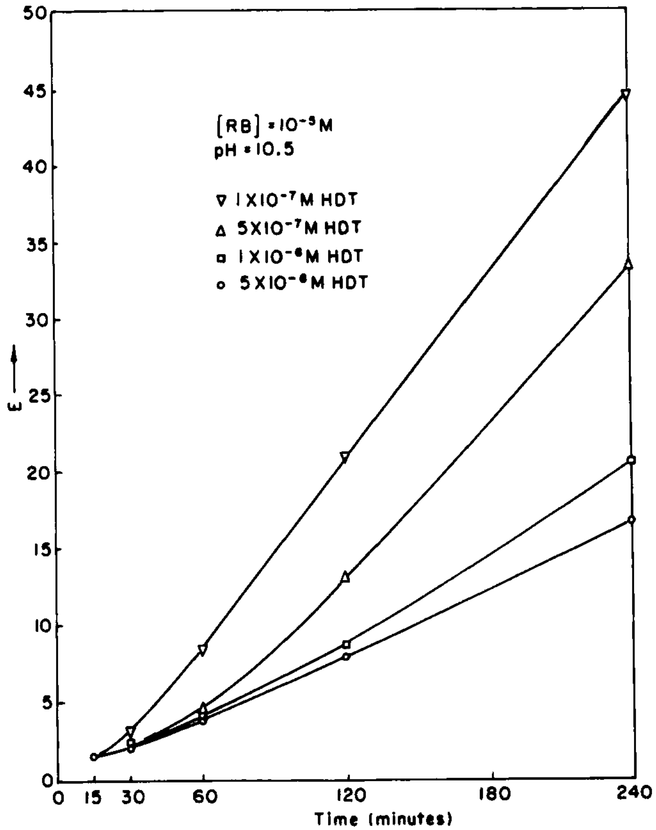


FIG. 5. Effect of HDT concentration on the rate of extraction of RB.

min the 5×10^{-7} *M* curve starts to diverge from the 10^{-6} *M* and 5×10^{-6} *M* curves and at 120 min the later two curves diverge from one another. This behavior is readily explainable from the results in Table 2. Above an initial HDT concentration of 4×10^{-7} *M* the *E* values for RB are independent of HDT concentration. Apparently the times at which the curves diverge in Fig. 5 are the times at which the HDT concentration in the aqueous phase decreases below the critical value.

In Fig. 5 it can also be seen that the rate of extraction of RB becomes constant after long gas bubbling times for initial HDT concentrations of 10^{-7} *M* and 5×10^{-7} *M* (i.e., the plots of *E* vs. time become linear). It can also be seen that the slopes of these two straight lines are, within experimental error, equal to each other. These results are also consistent with the data presented in Table 2. Examination of this table reveals that for an initial HDT concentration of 1×10^{-7} *M*, the percentage of RB extracted into the octanol phase in 60 min of gas bubbling is 40%. This percentage is equal to that extracted under the same conditions with no surfactant present. Thus in the long time periods for both the 10^{-7} *M* and 5×10^{-7} *M* initial HDT concentration experiments, the level of HDT concentration in the aqueous phase has decreased to the point that the surfactant no longer influences the removal of RB. For these long bubbling times, the rate of extraction becomes a function of the rate of formation of bubble surfaces, which is a constant for the experiments of Fig. 5, and accordingly the slope of the two straight lines become equal. It is expected that for longer gas bubbling times the plots of *E* vs. time for initial concentration of HDT of 10^{-6} *M* and 5×10^{-6} *M* will also become linear with slopes equal to those of the lower HDT concentration plots. In conclusion, therefore, the rates of extraction of RB at constant gas flow rate with varying initial concentrations of surfactant increase with gas bubbling time until they reach a constant limit equal to the rate of extraction of RB without surfactant. Eventually, of course, the rate of extraction of RB must decrease when a substantial portion of the RB has been extracted into the octanol phase.

The effect of HDT concentration on the percentage of MO extracted into the octanol phase in a 60-min gas bubbling time (5 ml/min flow rate) is quite different than the effect on the percentage of RB extracted. In Table 2 it can be seen that an increase in HDT concentration produces an increase in the amount of MO extracted. Presumably this result is due to the increased formation of surfactant-dye ion pair as the initial HDT concentration is raised.

A further interesting result of the effect of HDT concentration on MO extraction can be seen if, as in Fig. 6, we plot the percentage of MO extracted in the 1-hour period vs. HDT concentration. It can be seen in this figure that the % MO extracted is linear with initial HDT concentration up to 5×10^{-6} *M* HDT, beyond which the per cent extracted becomes smaller than that expected from a linear relationship. Part of the reason for this behavior can be understood by an examination of Figs. 7(a) and (b), which are plots of *E* vs. time of gas flow at varying concentrations of HDT. In Fig. 7(a) it can be seen that the rate of change of *E* with gas flow rate after 60 min

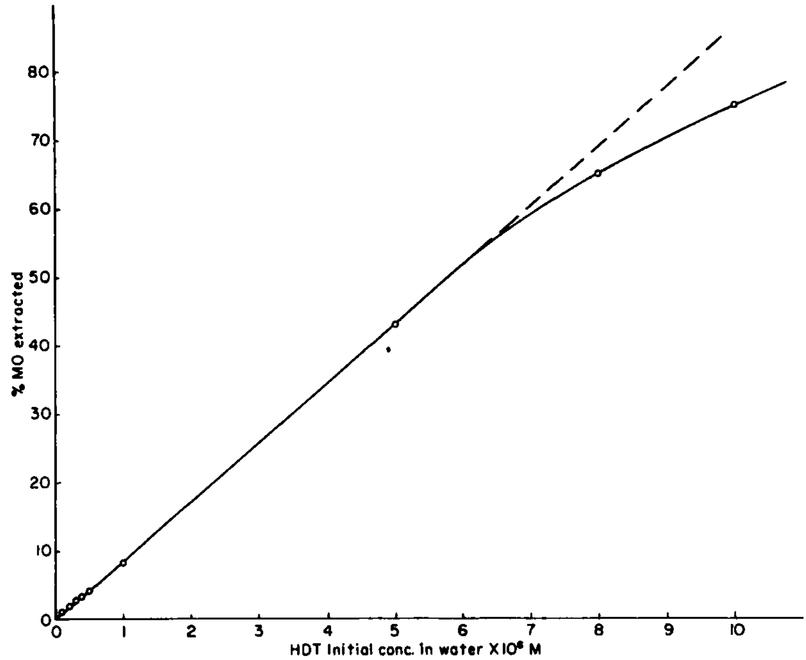
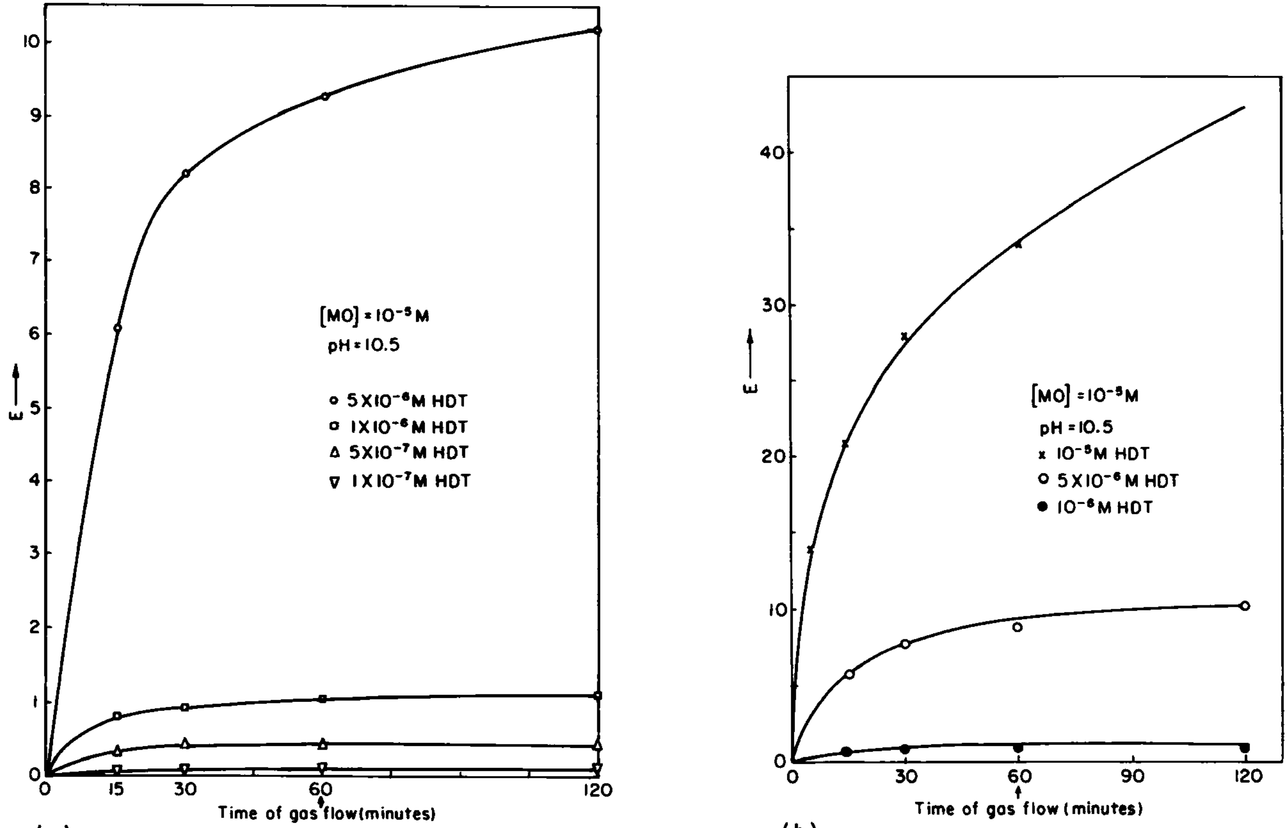


FIG. 6. Effect of HDT concentration on the extraction of MO, 10^{-5} *M* MO, pH 10.5.

bubbling time is negligible for HDT concentrations of 10^{-7} *M*, 5 × 10^{-7} *M*, and 10^{-6} *M*. Figure 7(b) indicates that the rate of change of *E* with flow rate at 60 min bubbling time is small for an HDT concentration of 5 × 10^{-6} *M* relative to 10^{-5} *M*. Thus the fact that the % MO extracted is no longer linear with HDT concentration above 5 × 10^{-6} *M* may be caused by the lack of sufficient surface generated to remove the ion pair substantionally. With longer gas bubbling times it is expected that the linear relationship would continue to higher initial HDT concentrations.

Comparison of Medium and Coarse Frits

Since the amount of gas-liquid surface generated in the aqueous phase has an important role in the sublation process, it was decided to test the effect of frit type on the *E* values of RB and MO for a given volume of gas passed through the column. For the extraction columns, Corning #39570 30-mm tubes with coarse, medium,



(a) (b)

FIG. 7. (a) Effect of HDT concentration on the rate of extraction of MO; (b) effect of HDT concentration on the rate of extraction of MO.

and fine porous glass frits were sealed to 45-mm Pyrex glass tubing, care being exercised not to heat the frits. Experiments indicated that excessively high pressures were needed to force gas through the fine frit and, therefore, it was decided to compare only the medium and coarse frits.

TABLE 3

Comparison of Coarse and Medium Frits[a]

Frit		E
Sublation of Methyl Orange[b]		
Coarse	60% MO_{oct}	19
Medium	75% MO_{oct}	34
Sublation of Rhodamine B[c]		
Coarse	11% RB_{oct}	0.8
Medium	18% RB_{oct}	1.4

[a] Gas volumetric flow rate 5.0 ml/min. Gas flow time, 60 min.
[b] 10^{-5} *M* MO, 10^{-5} *M* HDT; pH 10.5.
[c] 10^{-5} *M* RB, 10^{-5} *M* HDT; pH 10.5.

Table 3 presents the results of this comparison for both MO and RB. In both cases the conditions were 10^{-5} *M* dye, 10^{-5} *M* HDT at pH 10.5; gas flow rate 5.0 ml/min; and time of gas flow 60 min. It can be seen in Table 3 that the *E* values of the two dyes increase when changing from the coarse to the medium frit; in other words, the medium frit affords greater efficiency for the extraction process. The fact that the medium frit provides for the sublation of a greater quantity of material can be understood in terms of the amount of surface generated. Since the medium frit will produce smaller bubbles than the coarse frit, the amount of bubble surface generated in the aqueous phase for a given volume of gas will be larger for the medium frit. The larger the surface area generated, the more sites available for adsorption and consequently the larger the *E* values.

Comparison of Liquid-Liquid Extraction and Solvent Sublation

At first glance liquid-liquid extraction and solvent sublation may seem analogous, since both methods use two immisible phases; however, there are some very important differences for the two techniques. Liquid-liquid extraction is a partitioning process which requires intimate contact between the two liquid phases (usually by some shaking procedure). For the most part, separations and extractions are based on the attainment of solute equilibrium between the two phases, as reflected in the distribution coefficient, and equilibrium is often rapidly obtained.

Solvent sublation is a process that employs gas bubbles for mass transfer. Adsorption occurs on these bubbles, and during sublation there is a unidirectional flow of mass from the aqueous phase to the octanol phase. Indeed, the equilibrium distribution between the two phases will probably not be produced even at extremely long times when solute in the octanol phase diffuses back into the water. Since solvent sublation may be considered a nonequilibrium process, it may thus be possible to extract into the organic phase an amount of material greater than that required for equilibrium. There may be some solubility limit to the extent to which equilibrium distribution may be exceeded, but solute saturation of the octanol phase should not be a problem for the concentrations used in this work.

In liquid-liquid extraction, the relative volume of the two immiscible phases can be an important parameter in determining the relative amount extracted. Indeed, depending on the distribution coefficient, the removal of trace quantities of material from one phase may require a large volume of the immiscible second phase.

In solvent sublation, Sebba (*4*) has shown that the volume of 2-octanol does not effect the amount of material extracted from the aqueous phase. We have checked these results by examining the effect of volume of the organic phase on the rate of extraction of RB and MO. Runs were made with octanol volumes of 5, 25, 50, and 100 ml (aqueous phase volume always 300 ml) at a flow rate of 5 ml/min for a 1-hour gas bubbling period. The solution employed was 10^{-5} *M* MO, 10^{-5} *M* RB, and 10^{-5} *M* HDT at pH 10.5. The results are shown in Table 4, and it can be seen that the percentages of MO and RB extracted are independent of volume of octanol.

The fact that the volume of octanol does not affect the sublation process is quite reasonable, since for the most part mass transfer occurs from gas bubbles crossing the liquid-liquid interface, not from diffusion across this interface. Indeed, whereas in liquid-liquid extraction attempts are made to produce a great deal of liquid-liquid interface by agitation, in solvent sublation gas flow

TABLE 4

Effect of Volume of 2-Octanol[a]

Volume 2-octanol, ml	MO_{oct}, %	RB_{oct}, %
5	75	15
25	75	15
50	75	15
100	74	15

[a] System: 10^{-5} *M* MO, 10^{-5} *M* RB, 10^{-5} *M* HDT; pH 10.5; gas flow rate, 5 ml/min; gas flow time, 1 hour.

rates are so chosen that disruption of the water-octanol interface is minimal.

A direct experimental comparison was made between solvent sublation and liquid-liquid extraction. For this purpose 25 ml of octanol and a 300-ml aqueous solution of 10^{-5} *M* each of MO, RB, and HDT at pH 10.5 were used. In the solvent sublation experiments, nitrogen gas was bubbled through the solution for 1 hour and in the liquid-liquid extraction experiments, the solution was placed on a mechanical shaker for 1 hour.

It should be noted in the first place that an emulsion formed in both phases in the liquid-liquid extraction experiments, and that this emulsion only broke up on standing for 15 to 24 hours. Emulsion formation is a definite problem in the extraction technique, especially when using surface active agents. However, in solvent sublation no emulsion was observed for either phase. Thus solvent sublation allows the use of certain surface active complexing agents which cannot be used in liquid-liquid extraction.

The results of the direct comparison of the two techniques are shown in Table 5. Examination of this table reveals that for 60 min extraction time, a smaller percentage of MO and RB is extracted into the octanol phase by solvent sublation than by liquid-liquid extraction. It is also to be noted that while the difference in the percentage extracted for the two techniques is not large for MO, there is a significant loss in the percentage of RB extracted by solvent sublation. These results are due to the fact that the rates of extraction are considerably slower in solvent sublation than in liquid-

TABLE 5

Comparison of Liquid-Liquid Extraction and Solvent Sublation

Method	MO_{oct}, %	RB_{oct}, %	E	ϕ
Extraction of Methyl Orange[a]				
SS[b] (60 min)	75		34	
LLE[c]	89		97	
SS (720 min)	95		200	
Extraction of Rhodamine B[d]				
SS (60 min)		18	2.6	
LLE		84	63	
SS (720 min)		80	48	
Separation of MO and RB[e]				
SS (60 min)	75	18		17
LLE	89	84		1.7

[a] 10^{-5} *M* MO and 10^{-5} *M* HDT; pH 10.5.

[b] SS, solvent sublation; gas flow rate, 5.0 ml/min.

[c] LLE, liquid-liquid extraction; shaking time, 60 min.

[d] 10^{-5} *M* RB and 10^{-5} *M* HDT; pH 10.5.

[e] 10^{-5} *M* MO, 10^{-5} *M* RB, and 10^{-5} *M* HDT; pH 10.5.

liquid extraction, and that since the two dyes possess different mechanisms of sublation, MO is sublated more rapidly than RB.

It can further be noted in Table 5 that in 12 hours gas bubbling time 95% MO is sublated, whereas only 89% is removed by liquid-liquid extraction in 1 hour. If we assume that the values obtained in the liquid-liquid extraction experiment are close to the equilibrium distribution values, then it can be seen that the equilibrium distribution may be exceeded in solvent sublation, in which a surfactant-dye ion pair is removed, as we have previously stated. In the case of RB, 80% is sublated in 12 hours while 84% is removed by liquid-liquid extraction. Since the sublation of RB is caused by adsorption of the dye directly on the bubbles, it may well be that an aqueous-phase surface tension is reached after substantial removal of RB—and also HDT—at which only negligible amounts of the dye are removed. The sublation of RB at long time periods was not studied in enough detail to shed light on this point.

Finally, in Table 5 we have given data on the separation of the two dyes using both techniques. For 1 hour of extraction time it can be seen that the separation factor is 10 times larger for solvent sublation than for liquid-liquid extraction. This result can be attributed in large measure to the considerable decrease in the percentage of RB extracted by solvent sublation caused by the competition between HDT and RB for the gas-liquid interfacial adsorption sites.

CONCLUSION

Foam fractionation has found wide usefulness in several engineering fields, especially in those areas dealing with waste removal. The technique can also be used in analytical separations, when one wishes to remove and perhaps concentrate trace impurities. For example, Karger et al. (*1*) have developed a simple apparatus for analytical use employing total reflux. Foam fractionation, however, would appear to have one disadvantage in analytical work—a difficulty in selectively separating one solute from another. This difficulty arises from two sources: (1) in the formation of a foam, bulk liquid is entrapped in the plateau borders between the gas bubbles, and (2) when attempting to separate non-surface-active species, a large excess of foaming agent may be needed for production of the foam.

Ion flotation (*2*), as developed by Sebba, tends to counteract the above problems. In this method small doses of surfactant are added to a solution so that an unstable foam is produced. The foam breaks above the solution to produce an insoluble surfactant-solute product, which is prevented from returning to the bulk phase by the foam layer. This product is presumably free of other bulk species. In this method selectivity may be gained by adjustment of the charge on the non-surface-active solutes. For the case in which the solutes are of the same charge, preferential removal of one species may occur through the use of low concentrations of surfactant, such that only the most strongly formed ion pair of complex may be produced.

Ion flotation also presents problems for analytical separations. The concentration of surfactant must be high enough that a foam, albeit unstable, can be produced. Thus selective separations at solute concentrations below ca. 10^{-4} to 10^{-5} M are not possible by control of surfactant concentration. Also, collection of the insoluble product floating on top of the foam may not be quantitative. If it is decided to collect all the foam produced rather than just the insoluble product for quantitative purposes, then one may have poorer concentration of solute.

Sebba developed solvent sublation as an auxiliary technique to ion flotation, for use when persistent foams occurred. The sublation method, however, would also appear to possess advantages that foam fractionation and ion flotation do not have. In the first place, only gas-liquid interfaces are removed from the aqueous phase, without accompanying bulk liquid, as in foam fractionation. The octanol provides a convenient collection medium of the surfactant-solute ion pair which should be quantitative. Further, since it is clear that only a small volume of octanol is necessary for the successful operation of solvent sublation, the method has definite potential as a concentration technique.

Since in solvent sublation there is no longer the necessity for producing a foam, it should be possible to selectively remove ionic solutes from an aqueous phase at trace concentrations. The larger the formation constant of the surfactant-solute ion pair or complex, presumably the lower in concentration that one can operate solvent sublation selectively. Rates of removal at these low levels of concentration may be slowed sufficiently by use of large volumes and the slow generation of large bubbles (capillary bubbler).

Solvent sublation should be applicable to the separation of many different types of ionic solutes, both organic and inorganic. The non-surface-active ionic species can interact with an oppositely charged surfactant and be removed from the aqueous phase. The solvent sublation of methyl orange is an example of this procedure. On the other hand, surface-active species can be extracted without the use of an added surfactant. The solvent sublation of rhodamine B, without added cationic surfactant, is an example of this procedure.

Kinetic models of the solvent sublation of methyl orange and rhodamine B are currently being developed, and the effect of other parameters are being investigated. Development of solvent sublation to the separation of species of the same charge is also in progress. The results of this work will be presented at a later date.

REFERENCES

1. B. L. Karger, R. P. Poncha, and M. W. Miller, *Anal. Chem.*, **38**, 764 (1966).
2. F. Sebba, *Nature* **184**, 1062 (1959).
3. R. B. Grieves and D. Bhattacharyya, *A.I.Ch.E.J.*, **11**, 274 (1965).

4. F. Sebba, *Ion Flotation,* Elsevier, Amsterdam, 1962, Chap. X.
5. R. Rametta and E. Sandell, *J. Am. Chem. Soc.*, **78,** 3872 (1956).
6. A. B. Caragay and B. L. Karger, *Anal. Chem.*, **38,** 652 (1966).
7. E. Rubin and E. L. Gaden, Jr., *Separation Techniques* (H. M. Schoen, ed.), Wiley (Interscience), New York, 1962, p. 319.
8. A. J. Rubin, J. D. Johnson, and J. C. Lamb, III, *Ind. Eng. Chem. Process Design Develop.*, **5,** 368 (1966).

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