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Studies in the Mechanism of Sublate Removal by Solvent Sublation. Part I

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Summary

Solvent sublation, a method related to ion flotation, was studied by sublating hexadecyltrimethylammonium bromide and Methyl Orange into 2-octanol. It was shown that if the aqueous solution was saturated with 2-octanol, removals of Methyl Orange were much slower than with unsaturated solutions, because the 2-octanol tended to exclude collector from the bubble surface. The amount of Methyl Orange sublated was found to be different from that at liquid–liquid equilibrium, although the system reverted to the latter state if the sublation was discontinued and the solution was stirred. The organic phase retained any material passed into it and, other than the effects due to solubility, its presence had little influence on the processes occurring in the bulk of the aqueous solution. A detailed mechanism for sublate removal by solvent sublation is proposed.

INTRODUCTION

Ion flotation (*1–4*) is a process in which an ionic species, called the colligend, is removed from dilute solution by adding surface-active collector ions of a charge opposite to that on the colligend, and then bubbling an inert gas through the solution. If the concentrations of the collector and colligend are sufficiently high, a precipitate is formed and when gas is passed into the solution, the particles are floated out. At lower concentrations, no precipitate forms prior to the advent of gas, but instead collector ions adsorb on the bubbles and attract colligend

ions to them. When the bubbles reach the surface of the solution, a foam is formed in which a solid phase is deposited.

In each case the product adsorbed on the bubbles is known as a "sublate" and may either be a solid or a group of ions held together by coulombic attraction. The process of lifting the sublate to the surface of the solution is known as "sublation." Once the sublate has reached this surface, it forms a foam which can be removed mechanically; however, it is often more convenient to spread a layer of an immiscible organic solvent on the surface of the solution. No foam forms under these conditions, but the sublate is retained in the organic phase and is more amenable to quantitative removal. Sebba (*3*, *4*) has called this process solvent sublation and has encompassed within its definition not only the formation of true solutions but also of suspensions of sublate in the organic phase.

As few publications have dealt with solvent sublation, it will be worthwhile to survey the field at this stage, emphasizing those aspects of each paper that are relevant to the present discussion. In each case described, removal of the sublate occurred from a true solution of colligend and collector.

Most of the investigations made on solvent sublation have dealt with the case in which the sublate dissolves completely in the nonaqueous phase. The first such study was made by Karger, Caragay, and Lee (*5*), who sublated hexadecyltrimethylammonium bromide (HTMAB), Methyl Orange (MO), and Rhodamine B (RB) into 2-octanol. The pH of the solution was adjusted so that RB was zwitterionic, and hence uncharged, while MO occurred as an anion. The latter colligend, therefore sublated readily with the cationic collector HTMAB, whereas RB did not. Prolonged passage of gas resulted in the 2-octanol attaining a constant composition corresponding to 95% removal of MO as compared with 89% attained by liquid–liquid extraction. This experiment was conducted in a sublation cell with a medium porosity frit, the pores of which were 35 μ in diameter. The recovery attained after an arbitrary period of 1 hr was 75% irrespective of what volume of 2-octanol, between 5 and 100 ml, was used.

Sebba anticipated that the amount of sublate moved into the organic phase during solvent sublation could exceed that achieved by liquid–liquid extraction. The above results appear to vindicate this supposition although the system involving HTMAB and MO under the conditions chosen does not illustrate the effect well. This is because the equilibrium value of 89% is too close to 100% removal to

allow accurate measurement of the amount by which solvent sublation exceeds equilibrium.

With this in mind, Sheiham and Pinfold (*6*) examined the solvent sublation into 2-octanol of hexadecyltrimethylammonium chloride (HTMAC) alone; these authors used solutions 10^{-5} *M* with respect to this collector and followed its removal from the aqueous solution radioactively by adding a ^{14}C-labeled spike of HTMAC. The sublation cell used was of a type originally described by Sebba and contained a fine porosity frit, the pores of which were 10 μ in diameter. The bubbles (*7*) in such a cell were appreciably smaller than those produced by a medium porosity frit used by Karger et al. (*5*) and hence the area of gas–liquid interface passing through the aqueous phase for a given amount of gas was very much larger. Removal of collector into the 2-octanol layer was consequently more rapid and reached a constant value of 86% after 60 min.

On discontinuing the passage of gas, a stirrer was inserted into the aqueous phase and rotated at a speed such that stirring was efficient without unduly perturbing the octanol–water interface. Samples of the aqueous phase which were withdrawn after known time intervals showed that some of the collector which was dissolved in the 2-octanol returned to the aqueous solution. The equilibrium values ultimately attained for the distribution of HTMAC between the two phases were the same as those found in another experiment in which no bubbling was performed, but in which the aqueous solution was stirred in the same way as before. This illustrates conclusively that under certain conditions, solvent sublation allows a greater amount of sublate to move into a nonaqueous layer than is possible by liquid–liquid extraction. Clearly, however, if the amount of sublate removed into the nonaqueous layer is independent of the volume of the organic phase, the liquid–liquid equilibrium value will only be exceeded by sublation when the volume of the organic phase is small. With larger nonaqueous volumes, it is entirely conceivable that the liquid–liquid equilibrium value may exceed the sublation value.

A system in which the effects of excess colligend were examined was that due to Elhanan and Karger (*8*). Tri-*n*-octylamine hydrochloride and $FeCl_4^-$ ions were sublated into anisole under conditions where, due to excess of $FeCl_4^-$ ions, only 40% of the iron should have been removed. That slightly more iron than this was found in the anisole layer is attributed to the solubility of $HFeCl_4$ molecules in this solvent.

The solvent sublation of stoichiometric amounts of hexacyanofer-

rate(II) ions and dodecylpyridium chloride into 2-octanol, using a cell with a fine porosity frit, was undertaken by Spargo and Pinfold and is described in Part II of the present series (*7*).

Finally, it has been shown by Pinfold and Mahne (*9*) that solvent sublation, in which suspensions rather than true solutions of the sublate occur, can be useful in removing floated material. Precipitates that had been floated without the use of surfactants and were not soluble in nonaqueous solvents could be solubilized in such liquids by the addition of small quantities of surfactants to the organic phase prior to flotation. This technique may find practical applications but does not lend itself to quantitative study.

The purpose of the present investigation was to re-examine the solvent sublation of MO and HTMA into 2-octanol, with a view to elucidating the mechanism of the process. A cell with a fine porosity frit was to be used to determine how exposure of the aqueous solution to much greater bubble surface areas affected the process. Further, in the original study by Karger, Caragay, and Lee (*5*), both the 2-octanol and the water had been saturated with each other before use, and it was decided instead to employ pure solvents. A study of these results, together with those of Spargo and Pinfold (*7*), enable a plausible explanation for the mechanism of solvent sublation to be put forward.

EXPERIMENTAL

Materials

Hexadecyltrimethylammonium bromide (Matheson, Coleman and Bell) was recrystallized from an acetone–water mixture. Methyl Orange (Mallinckrodt Chemicals) and 2-octanol (Eastman Organic Chemicals) were used without further purification.

Apparatus

The sublation cell used was 9 cm in diameter, of 2 liters capacity, and contained a fine porosity frit, the average pore size of which was 10 μ; the frit from a Büchner was found to be suitable. A tap was inserted half way up the cell in order to allow the removal of samples from the aqueous solution for subsequent analysis. Before flowing into the cell, nitrogen gas was passed through a bulb of 2 liters capacity in order to dampen the effects of unexpected surges, and then through a flow meter. A flow rate of 10 liter hr^{-1} was maintained throughout this investigation. Although previously (*5*) the gas used

in sublation had been saturated with water before passing it into the cell, this precaution was found to be unnecessary with 1500 ml of water and was therefore not included in the present investigation.

Surface tension measurements were performed using a du Nouy tensiometer as supplied by Cenco, Inc.

Procedure

A volume of 1500 ml of a solution 10^{-5} M with respect to both MO and HTMAB was prepared, 10 ml of ethanol added, and the pH adjusted to 10.5 using sodium hydroxide. (The influence of ethanol on the rate of sublation will be explained later.) This solution was poured into the sublation cell, and a 10 ml sample was removed for analysis. A volume of 25 ml of 2-octanol was then spread on the surface of the solution, and the flow of gas was begun. Dispersion of gas throughout the aqueous solution was so rapid that sublation commenced at once; the zero of time, therefore, was regarded as that moment when bubbles first emerged through the frit. Samples of 10 ml were withdrawn through the tap in the cell at known time intervals during the run. The amounts of MO in these samples were determined by adding concentrated hydrochloric acid to reduce the pH to 1.6, after which the optical densities were measured at 506 μ using a Beckman DU-2 spectrophotometer. The percentage removal of the MO from the aqueous phase was determined by proportionately comparing these optical densities with that of the initial sample taken before sublation commenced. Each percentage removal quoted is the mean of several determinations; an estimate of the precision obtained is also given. The results are for systems which were in steady states, and each such determination included in a mean value was the average of several measurements made while the system was in the steady state.

RESULTS AND DISCUSSION

Effect on Sublation of 2-Octanol in the Aqueous Phase

As all previous experiments using a cell with a fine porosity frit had employed water and 2-octanol which were pure, it was decided to investigate the sublation of systems in which the liquids were mutually saturated. Figure 1 shows that by using 1500 ml of a solution 10^{-5} M with respect to HTMAB and MO, the removal of MO was much slower when the aqueous solution had been saturated with 2-octanol. With

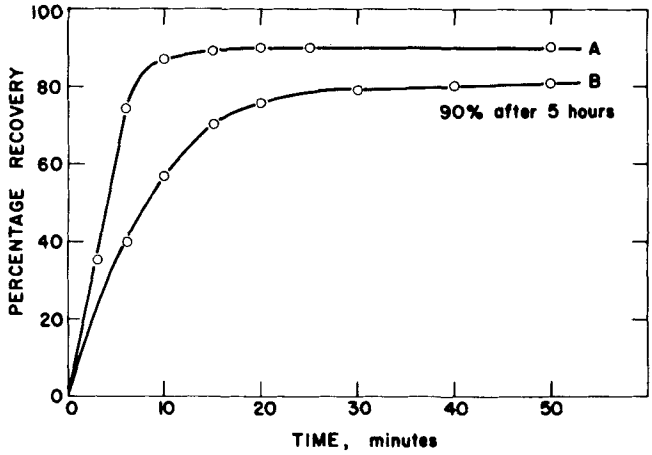

FIG. 1. The influence of 2-octanol in the aqueous phase on the rate of sublation. Conditions: 1500 ml aqueous solution of $10^{-5}M$ MO and HTMAB plus 10 ml EtOH; 25 ml of 2-octanol. A: No 2-octanol initially present in aqueous solution. B: Aqueous solution initially saturated with 2-octanol.

pure liquids, removal of MO reached a constant value after 20 min, but with saturated liquids this required 5 hr. These curves were found to be independent of whether or not the 2-octanol used had been saturated with water initially, and hence it can be assumed that the rate of sublation is controlled by the nature of the aqueous solution.

An explanation for this behavior can be given after consideration of the following experiments:

(a) A volume of 1500 ml of water containing 10 ml of ethanol but no MO or HTMAB was placed in the sublation cell and a 40-ml sample withdrawn through the side arm and retained in a shallow dish for the measurement of surface tension. Octanol was then spread on the surface of the water in the cell and the passage of gas was commenced in the usual way. Similar samples were withdrawn from the aqueous phase after known time intervals and their surface tensions were measured. As shown in Fig. 2, these values decreased gradually, approaching 34 dyne cm^{-1}, which is the surface tension of water saturated with 2-octanol. Clearly this solvent was dissolving in the aqueous phase.

(b) If 100 ml of ethanol, instead of 10 ml, were included in the solutions of HTMAB and MO in pure water, removal by sublation was appreciably slower. This effect, which is shown in Fig. 3, is similar to that for 2-octanol (of Fig. 1).

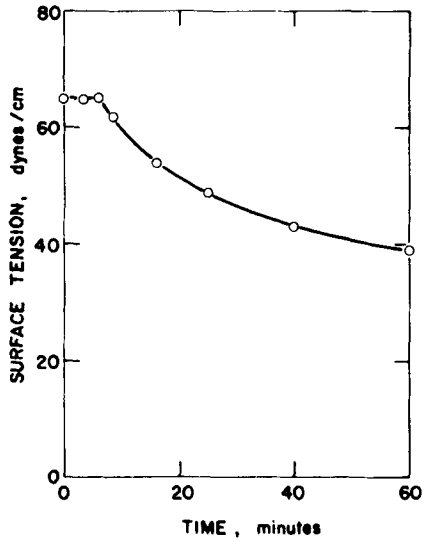

FIG. 2. The lowering of the surface tension of water during solvent sublation, due to 2-octanol dissolving in the water.

In explanation of the above behavior in Fig. 1, it is suggested that since 2-octanol is surface-active, it is adsorbed extensively on the gas bubbles passing through an aqueous solution saturated with this solvent. As its solubility in water is 1.3 g liter^{-1} at 25°C (*10*), a saturated aqueous solution contains about 0.01 mole liter^{-1} of 2-octanol. Because this concentration is 1000 times greater than that of the collector at the start of a run, it is likely that 2-octanol competes for sites on the bubble and thereby reduces the rate of sublation; the effect becomes more marked as the concentration of collector decreases during sublation. Such interferences also affect the sublation of aqueous solutions in which no 2-octanol had been dissolved initially. Although most of the colligend is removed in such cases within the first 10 min, removal of the remainder is slowed down by the increasing presence of 2-octanol at the bubble surface in the aqueous phase.

As ethanol is surface-active as well, it was to be expected that similar interferences would occur if it were present in sufficient quantities. The addition of 10 to 1500 ml of the aqueous solution is desirable in that the surface tension is lowered sufficiently to allow the formation of small bubbles; even if this volume is increased to 30 ml, the rate of sublation is not changed significantly. Excessive amounts of ethanol, however, clearly have a deleterious effect on the rate of removal, as shown in Fig. 3, and should be avoided.

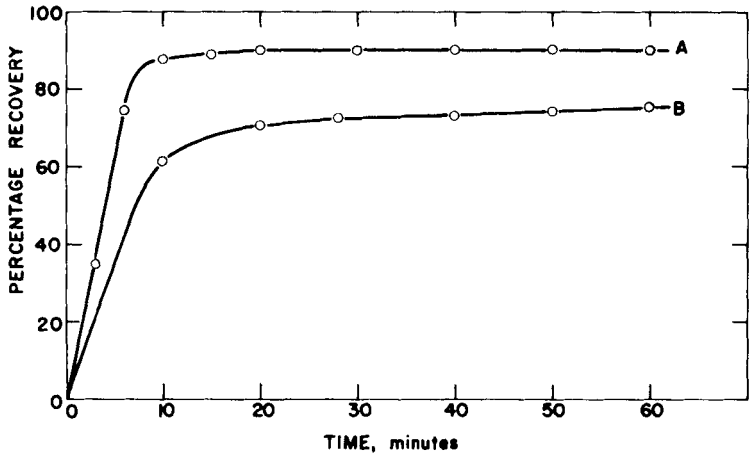

FIG. 3. The effect of ethanol on the rate of sublation. Conditions: 1500 ml aqueous solution of 10^{-5} *M* MO and HTMAB; 25 ml of 2-octanol. A: 10 ml EtOH added initially. B: 100 ml EtOH added initially.

Phenomena Occurring at the Liquid–Liquid Interface and in 2-Octanol

It was necessary at first to show that the amount of sublate that would be removed into 25 ml of 2-octanol from 1500 ml of a solution 10^{-5} *M* with respect to HTMAB and MO would not be sufficient to saturate the organic phase. This result would overcome the argument that incomplete removal of sublate from the aqueous solution could arise from limited solubility in the organic layer. To this end, 1500 ml of a solution 5×10^{-5} *M* with respect to HTMAB and MO was sublated into 25 ml of 2-octanol. Not only was the organic layer obviously deeper in color and hence more concentrated relative to the usual case of 10^{-5} *M* solutions, but the removal of MO from the aqueous solution was about 90% after 50 min. From this result it is evident that considerably more sublate had been accommodated in the same volume of 2-octanol than when using 10^{-5} *M* solutions, and the organic layer, therefore, was unsaturated during sublation of these less concentrated solutions.

In previous work, Karger et al. (*5*) showed that the amount of material removed from the aqueous phase after an arbitrary period of 1 hr was independent of the volume of 2-octanol present. To show that the same independence existed at any selected time during a run, the experiment in Fig. 1, Curve A, was repeated, except that the volume

of the organic layer was 75 or 100 ml, instead of 25 ml. Within experimental error, no change occurred in the curve under the new conditions and the removal at any stage during the sublation was therefore independent of the volume of 2-octanol used. In consequence, whether one exceeds the liquid–liquid equilibrium value during solvent sublation, or does not reach it, should depend on the ratio of the initial volumes of 2-octanol and water. If this ratio is small, as when using 25 ml of 2-octanol and 1500 ml of water, steady-state removal of colligend by solvent sublation should be in excess of the liquid–liquid equilibrium value. With larger volumes of 2-octanol, however, removal by solvent sublation will remain the same but the equilibrium value will increase and, with sufficient 2-octanol, will exceed the sublation value.

To compare more directly the amount of MO transported into the organic phase during solvent sublation with that required by the equilibrium distribution, the procedure devised by Sheiham and Pinfold (*6*), and described earlier, was used. Solvent sublation was performed under conditions similar to those in Fig. 1, and was continued until no further removal of MO occurred; the flow of bubbles was then stopped and a stirrer was inserted 2 in. below the 2-octanol layer. After 4 days of stirring the removals of MO into 2-octanol had declined to steady-state values of either 74% (±2%) or 84% (±2%), depending, respectively, on whether pure liquids or liquids saturated with each other had been used in the original solutions. If solutions of the same initial composition were not sublated but only stirred for 4 days in the sublation cells, the percentage extraction increased gradually to the same steady-state values. The results are shown in Fig. 4 for the sublation of solutions made originally from pure liquids; the curve obtained when using saturated solvents is essentially the same (i.e., no presaturation). These results indicate quite clearly that the extent to which MO is removed by solvent sublation is in excess of that attained in liquid–liquid extraction when 25 ml of 2-octanol is used.

If a nonsaturated solution that had been subjected to sublation and then stirred for 4 days was sublated for a second time, the behavior shown in Fig. 4 was repeated. There were, however, two essential differences between the first such cycle and the second: (a) The rate of removal of MO was slower during the second sublation, and (b) the equilibrium value attained after 4 days of stirring was 60%, which is lower than that after the first such period because the volume of 2-

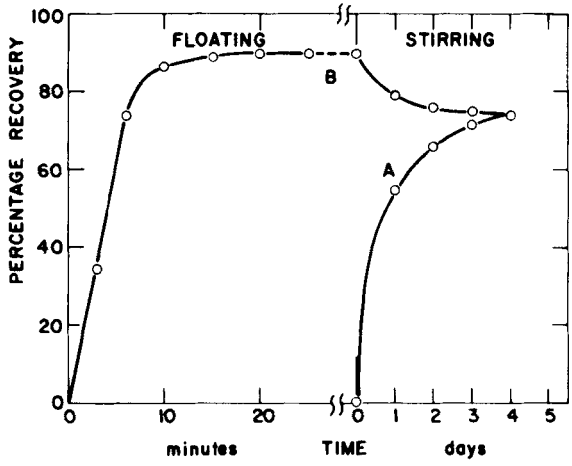

FIG. 4. The relation of solvent sublation to liquid–liquid equilibrium. Conditions: 1500 ml aqueous solution of 10^{-5} *M* MO and HTMAB plus 10 ml EtOH; 25 ml of 2-octanol. A: Attainment of liquid–liquid equilibrium by stirring. B: Liquid–liquid equilibrium exceeded by solvent sublation, but resorted by stirring.

octanol on the surface had been reduced. With less organic phase present, the amount of colligend it contains at equilibrium must necessarily be less.

It is of interest to consider the reasons for the decrease in volume of the 2-octanol layer during sublation. First, some of the solvent may be carried away as vapor with the nitrogen during the passage of this gas, or may be lost by evaporation during the 4-day stirring period. Second, emulsification of some 2-octanol probably occurs during this period. The extent to which each of these effects contributes is difficult to assess but most of the loss appeared to take place during the stirring period, and the final volume seemed to be independent of whether or not the solutions had been sublated. When pure solvents were used initially, a further loss occurred due to the solubility of 2-octanol in water, and the final volume of the organic layer was smaller. This explains why the equilibrium percentage removal was lower at 74% in such cases, as opposed to 84% when the solvents were mutually saturated.

Given the same initial conditions, the final volume of the surface layer appeared to be the same whether the solution was sublated and then stirred, or only stirred. Further, as the same percentage extraction

of MO occurred in both cases, it is believed that ultimately the same state of equilibrium was attained, irrespective of whether solvent sublation occurred or not.

Finally, an experiment was done using a solution of the sublate in 2-octanol which was about ten times more concentrated than that resulting from the usual sublation of 10^{-5} *M* solutions of HTMAB and MO. For convenience, this concentrated solution was prepared by the solvent sublation of a 10^{-4} *M* solution of the collector and colligend, the 2-octanol layer being subsequently removed and centrifuged. A volume of 10 ml of this layer was then added to the 2-octanol already present in a normal sublation which had proceeded for 50 min and had therefore attained a steady-state extraction value of 90%. Commencing 1 min after the addition, samples of the aqueous solution were withdrawn at intervals over a period of 20 min; analysis revealed no increase in MO content. Although the concentration of sublate in the organic layer had been increased fourfold by the sudden addition of excess sublate, no indication of the change could be detected in the aqueous solution. It is clear, therefore, that the nature of solvent sublation is such that the sublate is unable to return to the bulk aqueous solution once it has been contained in the organic phase. The next section discusses these results in terms of the mechanism of sublate removal.

The Mechanism of Sublate Removal by Solvent Sublation

The first attempt to explain solvent sublation was made by Sebba (*3*, *4*) and was based on the assumption that sublate moved across the water–octanol interface in one direction only, namely into the organic phase with the rising bubbles. By considering the results of the present investigation, together with those of Karger, Caragay, and Lee (*5*), Sheiham and Pinfold (*6*), and Spargo and Pinfold (*7*), it is clear that this is too simple an explanation and that additional features needed to be considered in proposing a satisfactory model. Sebba's ideas are true, however, to a first approximation and lead to the following conclusions:

(a) The amount of sublate removed from the aqueous solution does not depend on the volume of the organic phase. It is the gas–liquid interface of the bubbles that collects the colligend and transports this species to the organic layer, the latter therefore acting only as a

recipient. The present investigation has shown that removals at all times during sublation are independent of the volume of the organic phase.

(b) The organic phase accepts whatever sublate is passed into it. The present investigation shows that this is true to a first approximation. Two colligends can be separated, therefore, if one can be sublated to the exclusion of the other, since only that which is sublated will appear in the organic medium.

(c) Surface-active substances can be removed from aqueous solutions by solvent sublation with little chance of emulsification of the organic phase occurring in the water. This conclusion appears to be correct.

(d) In solvent sublation only a stoichiometric amount of collector is required for the complete removal of colligend from the aqueous solution. It has been shown (*5*, *7*), however, that this is not true and that an excess of collector is needed. This result probably arises from the fact that it is simply not possible to remove all the collector from very dilute solutions, and under such conditions a corresponding amount of colligend must remain behind as well.

One consistent omission by Sebba is any reference to the return of the sublate from the organic to the aqueous phase. At first sight this seems unreasonable, partly because the organic medium is often very concentrated with respect to sublate, and partly because water that had been dragged into the 2-octanol layer is observed to return to the aqueous phase in the form of droplets. Admittedly the interfacial area between the two solvents is not large, being that of the cross section of the sublation cell, but because of the marked turbulence caused by the bubbles, any sublate that moved downwards across the liquid—liquid interface should be rapidly carried into the bulk of the aqueous solution. These objections led Karger, Caragay, and Lee (*5*) to suggest an alternative mechanism of solvent sublation in which it was postulated that sublate moved in both directions across the liquid–liquid interface. A greater upward movement of sublate occurred because the flow of bubbles was in this direction. At the present time, however, it is necessary to suggest a different mechanism in the light of the following new evidence:

(a) It has been shown that at all stages during sublation, the amount of colligend removed at a given time is independent of the

volume of the organic layer. By the above model, however, the rate of return of sublate to the aqueous solution would depend on the concentration of sublate in the organic layer and consequently on the volume of the layer; the extent of removal would therefore not be independent of the volume, as found above.

(b) If the concentration of sublate in the organic layer is suddenly increased during sublation, no increase occurs in the concentration of sublate in the aqueous solution. If sublate were returning to the aqueous solution, a rapid increase in MO concentration would have been noticed.

(c) On discontinuing sublation and stirring the aqueous solution, it has been found that sublate moves back into the water if the equilibrium value is lower than the removal achieved by solvent sublation. The return, however, is very slow, and after 1 hr no noticeable change in the sublate concentration occurs. If sublate returned with ease, marked concentration changes would occur immediately after discontinuing sublation.

To take into account the above results, the following model is presented. The bubbles arriving at the organic–aqueous interface are small and have too little kinetic energy to overcome the interfacial tension; coalescence must occur before the bubbles transfer across the interface. Since the surface of the bubbles possess a zeta-potential due to adsorbed ions, mutual repulsions exist and coalescence is not rapid. The volume below the interface, therefore, contains many stationary bubbles, and the liquid trapped between them is effectively protected from the turbulence of the solution below. The stationary bubble layer is easily observed during a run.

Some of the liquid entrained in this interfacial region will be dragged into the organic phase by the larger bubbles moving upward. Collector and colligend contained in this water and adsorbed on the bubbles readily dissolve in the organic phase. When the bubbles finally burst into the atmosphere the water surrounding each of them form globules, which then returns across the liquid–liquid interface. Because of the small size of these droplets, a large area of organic–aqueous interface is exposed, and it is quite likely that liquid–liquid equilibrium is established between the two phases. Since the total volume of water in the organic phase is very small, the amount of sublate carried back into the aqueous solution is minimal. For example, referring to the system studied above, 1500 ml of water was required to retain 26%

of MO at equilibrium, the remaining 74% being found in the organic layer. When the volume of water is reduced to somewhat less than 1 ml, i.e., the water which is entrained in the 2-octanol, the actual quantity of sublate it contains is negligible. Herein lies an essential difference between solvent extraction and solvent sublation. In the former process the organic phase contents are in equilibrium with the bulk of the aqueous solution, while in solvent sublation, equilibrium exists with only the small amount of water that is entrained.

Because of the protection afforded by the stationary bubbles at the interface, the small amount of water that moves down from the organic layer is not carried into the bulk of the aqueous solution. Rather it is transported back to the organic phase in the form of layers around other bubbles and carries with it a small amount of sublate. A steady state is ultimately attained in which the amount of sublate traveling into the organic layers is equal to that carried back across the interface by the returning droplets.

CONCLUSION

With the additional understanding of solvent sublation brought forth from this paper and the following one (7), it is clear that this method is unique as an extracting process. First, the collection of sublate does not depend on the properties of a foam, as in such processes as ion flotation and foam fractionation. Further, the non-aqueous layer exerts no influence on the sublation process, at least in the early stages, and acts solely as an impassive collector of material. The layer does not need to be removed or its composition examined at any stage, the course of the sublation being conveniently followed by analysis of the aqueous solution. It should therefore be possible to study the parameters specifically affecting the flotation process with ease and confidence and under a wide variety of conditions.

On the industrial scale, solvent sublation has potential because of its ability to concentrate colligends from large volumes of aqueous solutions into small volumes of organic solvents. In fact, because the amount removed is independent of the volume of the organic phase, solvent sublation is able to concentrate more effectively than solvent extraction when the volume of the organic phase is low. Solvent sublation also has potential as a method of concentration in analytical determinations. Care must be exercised in this area, however, because part of the organic phase will evaporate during the sublation process.

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