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

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

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Summary

The influence on solvent sublation of changes in flow rate, temperature, and collector and colligend concentrations is determined. Recoveries increase with flow rate but not proportionately, increase with collector and colligend concentrations above the stoichiometric values, and decrease with rising temperatures. Sublations were followed by analyses of both aqueous and organic layers using radiotracer and spectrophotometric methods, respectively. The effects are explained by a currently accepted mechanism of the process and on the basis of excess surface area being available. The latter is shown to be true by photography and measurement of bubbles.

INTRODUCTION

The technique of solvent sublation (*1*) has been described in Part I of this series (*2*). The field has been adequately reviewed and a possible mechanism of the process has been suggested.

The purpose of the present communication is to report on four aspects of solvent sublation that had not been examined before, and which indirectly proved to be helpful in understanding the mechanism of the process. The experiments entail determinations of the total surface areas of the bubbles passed through the solution in unit time, and explain how sublation is affected by changes in the rate of gas

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flow, by temperature, and by the concentrations of the colligend and of the collector.

EXPERIMENTAL

Materials

Dodecylpyridinium chloride (DPC), obtained from Hooker Chemical Corporation, N.Y., was purified by refluxing twice with activated charcoal for 2 hr, first with absolute ethanol and then with acetone.

2-Octanol was obtained from British Drug Houses and used without further purification.

A stock solution of hexacyanoferrate(II) was prepared by dissolving the salt in water which had been boiled and saturated with nitrogen. It was stored in the dark under nitrogen, and remained stable for at least 2 days.

A solution of $K_4{}^{59}Fe(CN)_6$, to be used as a radioactive spike, was prepared by dissolving 10^{-4} mole of iron(II) chloride in 25 ml of water, adding 0.5 ml of active iron(III) chloride solution and 1.2×10^{-3} mole of potassium cyanide. The solution was heated to 70°C for 5 min, filtered, and made up to 100 ml. About 1 ml was used on each occasion; the actual volume was accurately measured, as cognizance had to be taken of the amount of hexacyanoferrate(II) added in this way. The ^{59}Fe was obtained from the Radiochemical Centre, Amersham, England, as iron(III) chloride in hydrochloric acid. Because of rapid exchange between Fe^{2+} and Fe^{3+}, the presence of a large excess of iron(III) chloride ensured that essentially all the activity occurred as Fe^{2+} ions.

Apparatus

Two types of sublation cells were used, depending on whether or not they contained radioactive solutions. Both were 9 cm in diameter, of 2 liters capacity, and contained fine porosity frits, the average pore size of which was 10 μ. The cell containing active material (cf. Fig. 1a) had the following additional features. It was constricted at the top to prevent the loss of contaminating material during sublation, and contained a ground-glass joint (A). On completion of a sublation experiment, the apparatus shown in Fig. 1b was fitted to the joint and the contents of the cell removed in a stream of water. A side arm,

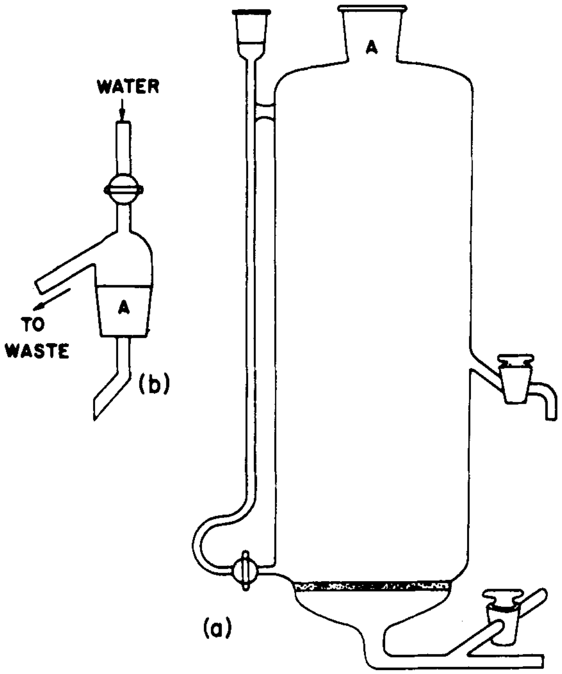

FIG. 1. (a) The sublation cell. (b) Attachment used for discharging radioactive solutions.

entering the cell just above the frit, was used to introduce the collector in the form of an ethanolic solution. A tap in the base of the cell allowed the safe removal of any radioactive solution that inadvertently leaked through the frit; another tap in the side of the cell was used for the removal of samples of the aqueous solution.

Before flowing into the cell, nitrogen gas was passed through a bulb of 2 liters capacity to dampen the effect of unexpected surges, then through a flow meter, a copper heat-exchanging coil, and a bubbler to saturate the gas with water. When the effect of temperature was being investigated, the cell, the heat-exchanger, and the bubbler were immersed in a water thermostat, the temperature of which could be controlled to within 0.2°C. For other measurements, all of which were at 25°C, the cell and gas line were contained in a fume chamber, the temperature of which did not fluctuate by more than 1°C.

The photographs taken of bubbles were made using a microscope and camera, operated in conjunction with a synchronized flash unit.

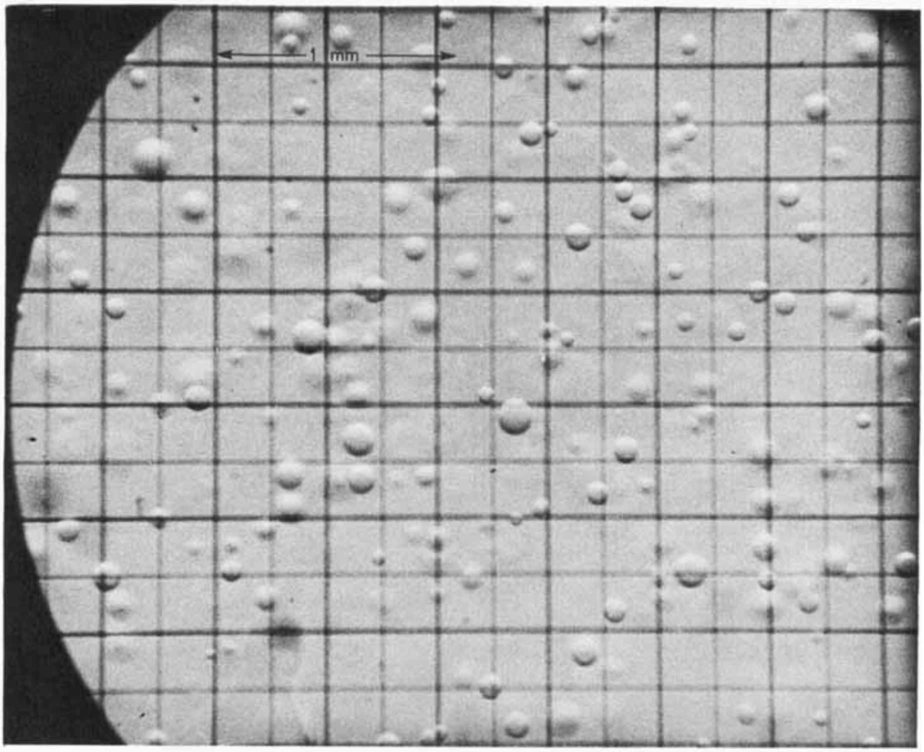

FIG. 2. Bubbles in sublation cell. Flow rate: 2 liters hr^{-1}.

The microscope was fitted with a graticule which was ruled in a pattern of regular squares The image of this graticule became part of the photograph, as shown in Figs. 2–4, and afforded a means of estimating the bubble diameters. This was done by photographing a wire of known diameter against the background of the graticule, and thereby obtaining a scale factor for converting measurements on a photograph to actual distances. The photographs were made using Kodak Plus-X-Pan film and a fine-grain developer.

Procedure

All sublations were performed using 20.00 ml of 2-octanol and, unless otherwise stated, 1500 ml of an aqueous solution containing 5×10^{-6} g ion of $Fe(CN)_6^{4-}$ and 2.0×10^{-5} mole of DPC. The stoichiometric ratio of 1 to 4 for the concentrations was chosen, as recoveries

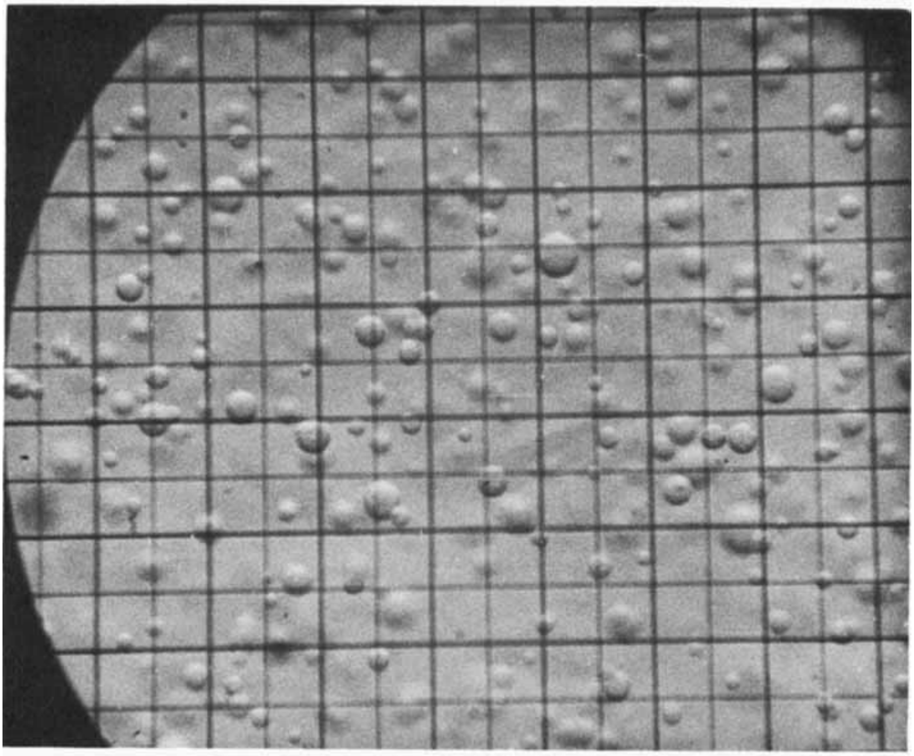

FIG. 3. Bubbles in sublation cell. Flow rate: 6 liters hr^{-1}.

under these conditions were most sensitive to changes in the parameters being investigated. The collector was added as an ethanol solution, 20 ml of which contained the 2.0×10^{-5} g ion of the DPC required. Recoveries were independent of the pH of the aqueous solution within the range 3–11.

When the spectrophotometric method of analysis was used, the procedure adopted was as follows: the solution of collector and colligend was placed in the sublation cell and a layer of 2-octanol was spread on the surface. Sublation was continued at a predetermined flow rate for a known time, after which about 10 ml of the organic layer was withdrawn, centrifuged to remove suspended water, and the optical density measured in 4-cm cells at 420 mμ. Prior to such determinations, a calibration curve had been prepared by sublating solutions of different colligend concentrations, each of which contained 48 times as much collector as colligend. This excess was chosen on the basis of

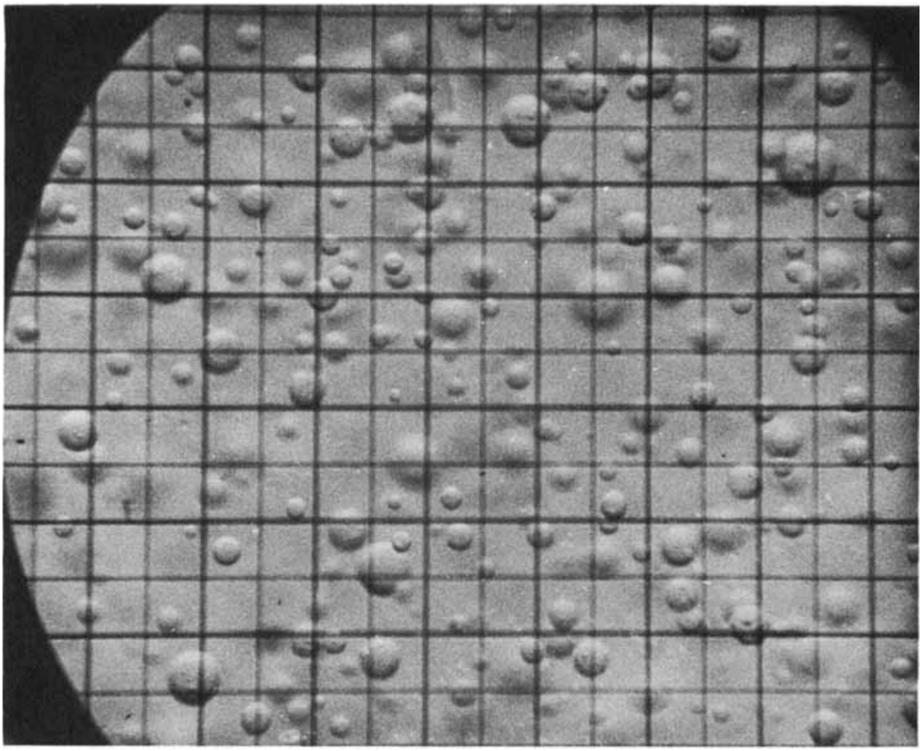

FIG. 4. Bubbles in sublation cell. Flow rate: 10 liters hr^{-1}.

Fig. 10 which shows that sublations were complete when the ratio of collector to colligend was 12 times that for stoichiometric conditions. [The calibration curve was linear and may be plotted knowing that sublation of 6.0×10^{-6} mole of hexacyanoferrate(II) resulted in an optical density of 0.47.] In other cases the percentage removal of colligend was found by comparing the actual amount of colligend sublated, as determined from the calibration curve, with the total amount originally present. The precision of the method is not good, the deviations of determinations made under any one set of conditions being within ±10% of the mean value; by repetition of the determinations, however, the mean values obtained fell on well-defined curves (cf. Figs. 8–10). An inherent weakness of the method is that the calibration curve was determined under conditions different to those extant for other solutions.

A different procedure was used when radioactive measurements were made. The colligend solution was placed in the sublation cell, a known volume of "spike" was added, the solutions were mixed by the passage of gas for a few minutes, and a 10-ml sample was withdrawn through the side tap. The collector solution was then placed in the side arm of the cell and gently blown into the main chamber. The tap in the side arm was closed, 20 ml of 2-octanol was spread on the surface using a pipet, and sublation was begun. Samples of the aqueous solution were withdrawn at known times thereafter, and the rate of γ-emission from 5.00 ml of each was measured. The percentage recovery of colligend was determined by proportionately comparing the counting rate of any sample with that of the one taken before sublation. The precision obtained by this method was within 5%.

RESULTS AND DISCUSSION

Determination of the Gas–Liquid Interfacial Area

A microscope and a camera were mounted next to the sublation cell, halfway up from the frit, as shown in Fig. 5. Ten minutes after commencing a sublation in which gas was flowing at 2 liter hr^{-1}, four pictures were taken at intervals of about 5 sec; the procedure was repeated at flow rates of 4, 6, 8, and 10 liter hr^{-1}. Typical examples of these pictures are shown in Figs. 2–4, from which it can be seen that

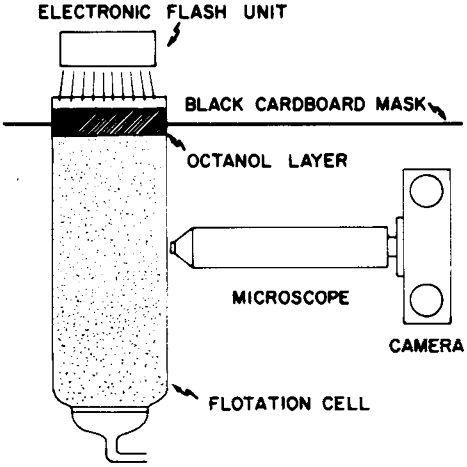

FIG. 5. Equipment used in the photography of bubbles.

the bubbles are spherical and very small; a distance of 1 mm in the cell corresponds to the sum of the sides of 4.3 adjacent squares on a photograph. A measurement was made of the diameter of any bubble for which the outline was reasonably well-defined, and in this way about 400 bubbles were examined at each flow rate. By use of a scale factor, determined as described above, the actual diameter of each bubble was calculated and hence its volume and surface area. From this data the ratio of the total volume to the total surface area for the bubbles examined was obtained. Knowing the flow rate and making the following assumptions, all of which are reasonable, the total surface area of bubbles formed in unit time was calculated: (a) that 400 bubbles are representative of the whole assembly, and (b) that no change occurs in the distribution of bubble sizes during sublation or with height above the frit. The results given in Table 1 are the first for a sublation cell with a fine porosity frit, and show that the areas involved are remarkably large. For example, during 50 min of sublation at 10 liter hr^{-1} the total bubble area formed was 336 m^2.

TABLE 1

Total Surface Area Formed per Minute at Various Flow Rates

Gas flow rate (liter hr^{-1})	2	4	6	8	10
Number of bubbles investigated	293	415	463	434	446
Volume of bubbles (mm^3)	0.141	0.241	0.354	0.357	0.536
Surface area of bubbles (mm^2)	8.18	12.9	17.2	16.7	21.7
Total surface area passed into the cell per minute (m^2 min^{-1})	1.93	3.57	4.85	6.20	6.72

Table 1 also shows that although the flow rate increases 5-fold from 2 to 10 liter hr^{-1}, the surface area formed per minute only increased 3.5 times. The effect is explained by changes in the distribution of bubble diameters that occur as the flow rate is increased (cf. Figs. 2–4 and 6). Each curve in Fig. 6 gives the number of bubbles of any given diameter that were determined from the photographs made at any one flow rate. Because the number of bubbles measured at each flow rate was different, the curves in Fig. 6 have been adjusted proportionately so that each corresponds to an arbitrarily selected number of 470 bubbles. In addition, the curve corresponding to 6 liter hr^{-1} has been omitted for clarity; its position is between that for 4 and 8 liter hr^{-1}.

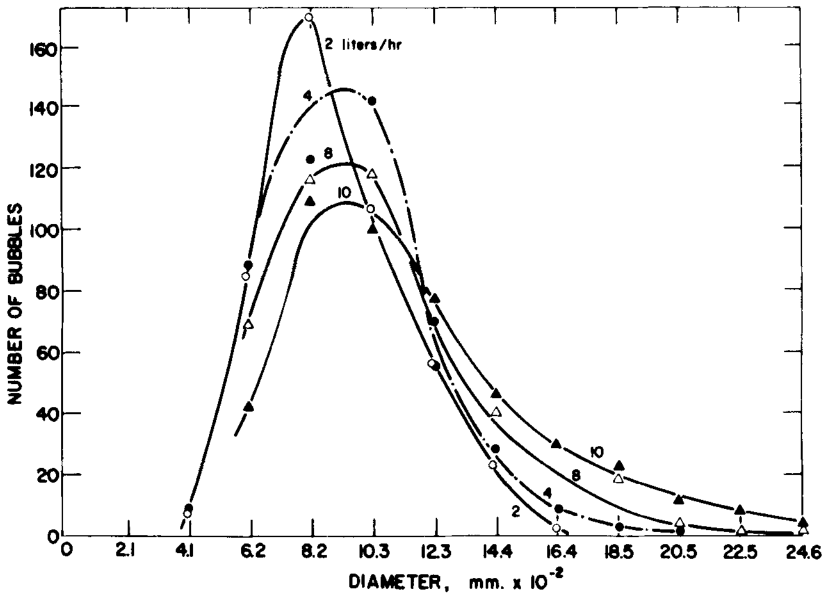

FIG. 6. Distribution of bubble diameters at various flow rates.

The data contained in Table 1 and Fig. 7 can be used to obtain an estimate of the average area of bubble surface available to each collector ion. This quantity, given the symbol θ, is obtained by dividing the total number of such ions that are sublated, into the total surface area available to them. The values of θ obtained are only approximate for the following reasons:

(a) θ increases as sublation proceeds because whereas the total amount of collector which is sublated approaches a constant value, the total area of the gas–liquid interface passed into the solution increases with time.

(b) In the present investigation the number of collector ions sublated was assessed by the extent of removal of the colligend, and thus no cognizance was taken of collector that sublated independently.

(c) For a short period at the beginning of the flotation, the amount of gas entering the cell was greater than that leaving it, as the population of bubbles built up to its steady value. An area of gas–liquid interface larger than that actually used to sublate the collector was therefore substituted in the calculation.

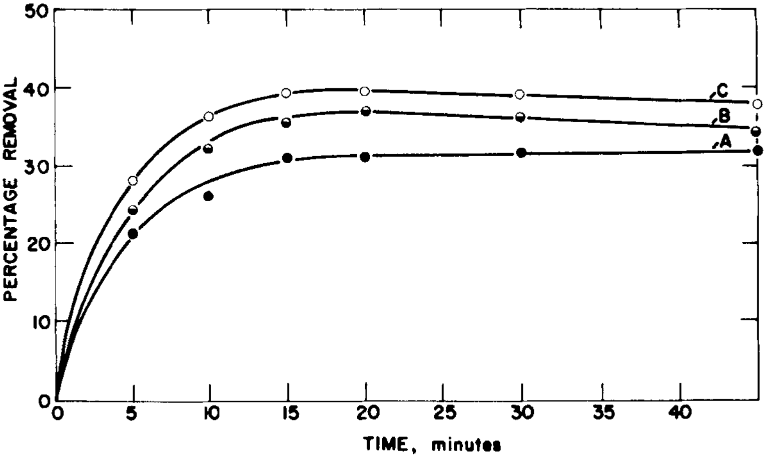

FIG. 7. Removals during sublation at various flow rates (radioactive method). Curve A: 2 liter hr^{-1}; B: 6 liter hr^{-1}; C: 10 liter hr^{-1}.

Each of these factors leads to a value of θ that is too high but from which meaningful deductions can nevertheless be made.

The errors incurred by factors (b) and (c) are not great. For example, the tendency of a multivalent ion such as $Fe(CN)_6^{4-}$ to be sublated is appreciably greater than that for a Cl^- ion, which is singly charged (*1*). The assumption, therefore, that the extent of removal of collector can be assessed by that of $Fe(CN)_6^{4-}$ ions is probably true, at least for the early stages of sublation. Further, the volume of the aqueous solution increased by 60 ml on commencing sublation at 10 liter hr^{-1} and this is necessarily the volume of the bubbles present. The surface area of these bubbles was 2.4 m^2 which was 7% of the area passed into the solution within the first 5 min. Errors of this magnitude are not large enough to influence the conclusions drawn from the results.

In deciding whether or not the surfaces of the bubbles are saturated with collector, the minimum value of θ is required at the lowest flow rate used. Because θ increases with time, this value will be the average over the shortest period measured from the commencement of sublation. From Fig. 7, Curve A, 21% of the colligend, and hence of the collector present initially, was removed in the first 5 min of sublation at 2 liter hr^{-1}. As the collector present initially in 1500 ml was 2.0×10^{-5} g ion, the amount removed was 4.0×10^{-6} g ion; from Table 1 the surface area passed into the cell in 5 min was 9.65 m^2, which gives a value of 400 Å^2 for θ (cf. Table 2). A shorter period of time is clearly desirable but as no measurements of the percentage removal had been made within the first 5 min, only interpolated values were available. (Measurements made too soon after the commencement of sublation are unreliable because a finite time is required to establish a constant flow of gas.) If interpolated values are accepted, 6% of the collector was removed in 1 min, giving a value of θ of 280 Å^2.

TABLE 2

Effective Area Occupied by a DP$^+$ Ion on the Bubble Surface

Gas flow rate (liter hr^{-1})	2	4	6	8	10
θ (average value over the first 5 min of sublation) (Å^2)	400	690	840	970	1000

As orientations of DP$^+$ ions on a bubble are unknown, the area occupied by an ion in a condensed film cannot be assessed. It must, however, be considerably less than 280 Å^2, which suggests that the bubble surfaces are not saturated with collector at any time after the first minute of sublation. The period during which the bubbles may be saturated, if this occurs at all, is therefore appreciably less than 1 min, which is an insignificant fraction of the time required to reach a steady state of removal. This result, that the bubbles are unsaturated with collector at virtually all times during sublation, will be used in subsequent sections.

Effect of Flow Rate on Sublation

The rate at which $Fe(CN)_6^{4-}$ ions are sublated was found to increase with flow rate. The effect is shown in Fig. 7, for which the analytical determinations were made on the aqueous solution using the radiotracer method. (Curves for 4 and 8 liter hr^{-1} have been omitted for clarity but lie between those for 2 and 6, and 6 and 10 liter hr^{-1}, respectively.) If, instead, the extent of removal was followed by optical analysis of the 2-octanol layer, curves of the same form were obtained. The recoveries measured by each method after 15 min of sublation at various flow rates are shown in Fig. 8; this time period was chosen because it corresponds closely to the maximum recovery attained at

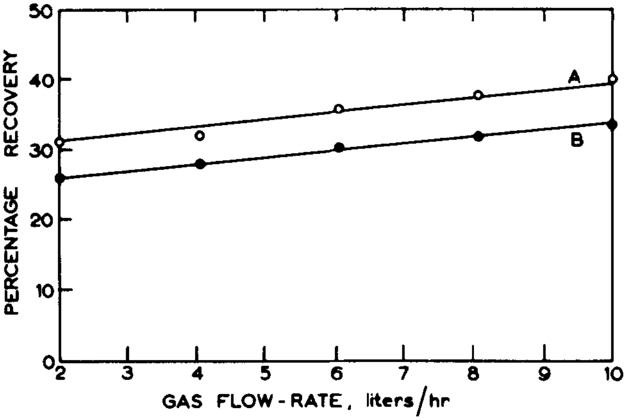

FIG. 8. Maximum recoveries attained at 25°C for various flow rates. Curve A: Analysis of aqueous solution using radiotracer techniques. Curve B: Analysis of 2-octanol layer using spectrophotometric method.

each flow rate. It is clear that the radiotracer technique gives higher results, but this could be due to uncertainties in the analytical procedures involving nonradioactive solutions. The reliability of the optical method, for example, is weakened by the fact that the calibration curve is determined under conditions different from those for other measurements. The significant point, however, is that the differences are the same at all flow rates, and this, taken with the fact that the curves referred to above are independent of which layer is analyzed, suggests that sublate is transported rapidly from the aqueous to the organic layer and does not accumulate at the interface. If such accumulation occurred, the rate by which the concentration of colligend increased in the 2-octanol would be less than that by which it decreased in the aqueous phase, and the above investigation shows that this does not happen.

A further significance of the above result, if it were shown to be true generally, is that solvent sublation can be followed by the analysis of only one of the liquid phases. This practice has been used expediently in the past but without justification because the efficiency with which sublate is transferred across the liquid–liquid interface was not known. Of the two phases, analysis of the aqueous solution is much more satisfactory, particularly by radiotracer methods. The uncontrollable loss of organic solvent during sublation reduces the value of analyzing this layer.

It is not surprising that greater flow rates lead to higher recoveries because a larger area of gas–liquid interface is available and collection is facilitated. The recoveries, however, do not increase by as much as the surface areas passed into the cell (cf. Fig. 7), probably because the bubbles are not saturated with sublate; even at the lowest flow rates, plenty of surface area is available. The disproportionate increase is not a consequence of the greater amount of water which is dragged into the organic layer by the larger number of bubbles passing through at higher flow rates. The amount of water involved is insignificantly small and, in any case, it does not return to the bulk of the aqueous phase (*2*). Other significant features of Fig. 7 are that (a) the percentage removals attained are well below the value of 100% which is theoretically possible and (b) the removal of $Fe(CN)_6^{4-}$ ceases after about 15 min. of sublation, regardless of the flow rate.

In explanation it is suggested that because four adsorbed DP^+ ions are required to hold each $Fe(CN)_6^{4-}$ ion to a bubble in a state of electrical neutrality, the formation of such groups of five ions, or pentads, becomes more difficult as fewer DP^+ ions are available in the solution. In addition, 2-octanol dissolves in the aqueous phase as sublation proceeds and these molecules adsorb on bubbles to an increasing extent. Their presence serves to keep the DP^+ ions apart and further hinders the formation of pentads. The sublation of $Fe(CN)_6^{4-}$ therefore ceases, although appreciable amounts of this ion remain in solution. The removal of DP^+ ions probably continues in partnership with the Cl^- ions present, although this process is known to be slow (*3*).

The rate at which 2-octanol dissolves in the aqueous solution is probably independent of flow rate due to compensating effects. The rate of solution, for example, will be greater the higher the flow rate, but the rate of removal by sublation also increases. Interference by 2-octanol in the present system is therefore probably independent of flow rate, and as this interference is a likely reason for the cessation of sublation, all removal ceases at the same time regardless of the rate at which the gas flows.

If sublations were discontinued after reaching their maximum values, and a stirrer was inserted below the organic phase as described previously (*2*, *3*), the sublate gradually returned to the aqueous solution and approached 15% removal, which was the value attained by liquid–liquid extraction. Unfortunately, the solution was not sublated a second time, which, contrary to the behavior of singly-charged colligends (*2*), should have resulted in no further removal of $Fe(CN)_6^{4-}$ because by then the solution would have become saturated with 2-octanol.

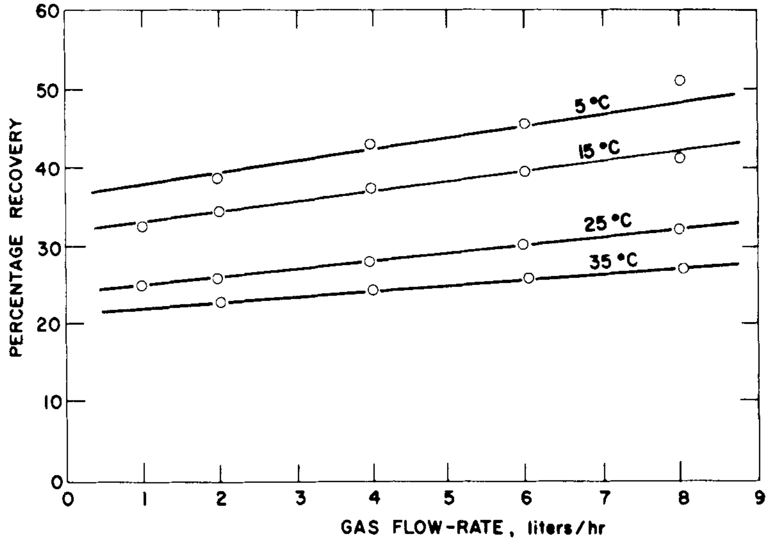

FIG. 9. Maximum recoveries attained at various flow rates and temperatures. (Spectrophotometric method.)

Effect of Temperature on Sublation

As shown in Fig. 9, the efficiency of sublation varies inversely as the temperature; spectrophotometric measurements were made 30 min after the start of sublations performed at different flow rates and at temperatures of 5, 15, 25, and 35°C. The results are readily explained in that adsorption is an exothermic process and a decrease in temperature therefore leads to greater concentrations of DP^+ ions on the bubbles and to better collection. As no previous study of the effects of temperature on sublation has been made, it is not known which other changes in the properties of the system have the most marked influences. The viscosity of the aqueous phase may be the most important such property, as its increase with temperature, and hence its effect on the speed of the bubbles, is appreciable. Such changes may, in turn, affect the rate with which bubbles pass across the octanol–water interface and also their residence time in the aqueous solution.

Effect of Excess Collector and Colligend on Sublation

The left- and right-hand parts of Fig. 10 show the effects of excess collector and colligend, respectively; the flow rate was 10 liter hr^{-1}

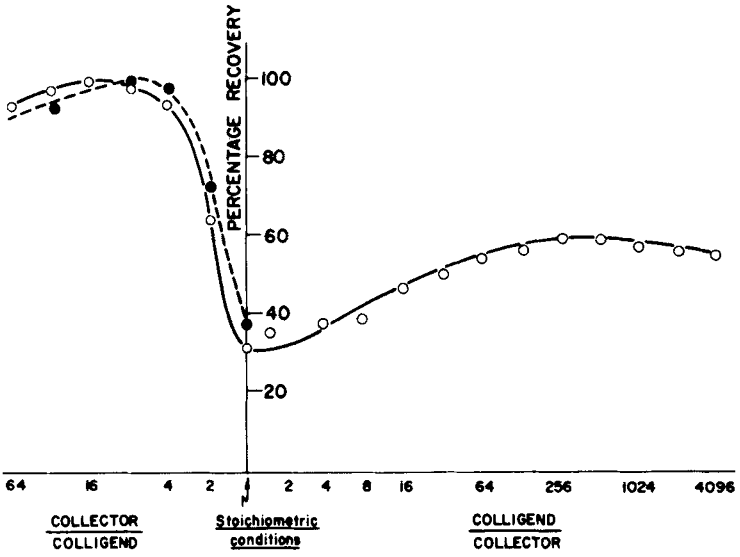

FIG. 10. Maximum recoveries attained when collector or colligend was in excess. Full curve: Spectrophotometric method. Dotted curve: Radiotracer method. (Flow rate: 10 liter hr^{-1}.)

and measurements were made after 30 min of sublation. For the curves on the left a constant amount of 5×10^{-6} g ion of $Fe(CN)_6^{4-}$ was present in 1500 ml of solution, and the collector was increased in multiples of the stoichiometric amount. A collector-to-colligend ratio of 2, for example, implies that 4×10^{-5} g ion of collector was present in 1500 ml, i.e., twice the stoichiometric amount. For the curves on the right, 2×10^{-5} g ion of DPC was maintained in 1500 ml and colligend was increased in increments of 5×10^{-6} g ion. A colligend-to-collector ratio of 4, therefore, means that 2×10^{-5} g ion of both collector and colligend were present. Measurements were made by both the spectrophotometric and radiotracer methods although the latter was not used with excess $Fe(CN)_6^{4-}$ because the fraction of this colligend removed by sublation, decreased rapidly as its concentration was increased. The fraction of radioactive material removed necessarily decreased at the same rate and the difference soon became too small to measure accurately.

It is clear from Fig. 10 that complete removals of colligend under the given conditions require a marked excess of collector. It is not surprising that collection improves as increasing amounts of DPC are added, because collector ions are then more closely packed on the bubble surface and formation of pentads is facilitated. At higher concentrations of collector, recoveries decline and removal of $Fe(CN)_6^{4-}$ is not complete. This may be the result of saturation of the organic layer with DPC, and the consequent deposition of $(DP)_4Fe(CN)_6$ at the liquid–liquid interface; more simply, it may arise from interference by Cl^- ions in the transfer of $Fe(CN)_6^{4-}$ ions across the interface. That values recorded by the radiotracer method decline more steeply at high collector concentrations than those of the optical method may be due to slight emulsification of the organic layer. Small losses of this layer will not influence the optical determination, but return of radioactive material to the aqueous solutions results in lower values by the tracer method. It is clear from the above that whereas excess collector is necessary for complete removal, too much of it is deleterious.

On adding excess colligend, recoveries increase but to a much smaller extent and do not reach 100%. This is not surprising because the removal of collector under the present circumstances depends on the extent to which DP^+ ions adsorb on the bubbles and on how closely together they are packed, neither criterion of which will be greatly influenced by the concentration of colligend. That recoveries ultimately decline at high colligend concentrations may be due to precipitation of $(DP)_4Fe(CN)_6$, the particles of which will not float well because of the appreciable adsorption of $Fe(CN)_6^{4-}$ ions, which renders the surfaces hydrophilic.

CONCLUSION

It is evident that solvent sublation has many interesting features and is amenable to further investigation. For example, there are clear indications that the process is more efficient at low temperatures, which makes further study necessary in this direction. Also, no consideration has been given in the past to the shape of the cells used. As solution of the organic layer retards the process, the use of tall, thin cells, which reduce this tendency, may lead to faster sublations. More extensive photography of bubbles at various times during sublations, performed under different conditions, may determine the extent to which bubbles coalesce and also provide a better understanding of how collector ions pack together on bubble surfaces. For stationary surfaces, a considerable period is required for the formation of a condensed film, but it is not known how these conditions alter when the gas–liquid interface moves rapidly through a turbulent solution. Finally, no thorough understanding of solvent sublation is possible without studying the removal of both the colligend and collector. Such an investigation has not yet been done, although the radioactive labeling of both species, and the determination of each in the presence of the other, is quite feasible.

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