Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Solvent Sublation of Hexadecyltrimethylammonium Chloride

I. Sheiham[a][b]; T. A. Pinfold[a]
[a] DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG, SOUTH AFRICA [b] Department of Civil and Municipal Engineering, University College London, London, England

To cite this Article Sheiham, I. and Pinfold, T. A.(1972) 'The Solvent Sublation of Hexadecyltrimethylammonium Chloride', Separation Science and Technology, 7: 1, 43 — 50
To link to this Article: DOI: 10.1080/00372367208058970
URL: http://dx.doi.org/10.1080/00372367208058970

SEPARATION SCIENCE, 7(1), pp. 43–50, 1972

The Solvent Sublation of Hexadecyltrimethylammonium Chloride

I. SHEIHAM* and T. A. PINFOLD

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
UNIVERSITY OF THE WITWATERSRAND
JOHANNESBURG, SOUTH AFRICA

Summary

The extent to which hexadecyltrimethylammonium chloride is removed from 10^{-5} M solutions by solvent sublation into 2-octanol is compared to the extraction achieved by equilibrium distribution between the two phases. A comparison is also made between the rates of removal by solvent sublation and by foaming, which shows the former process to be slower but to be preferable if the foams are unstable. The findings are in keeping with a mechanism of solvent sublation published previously.

INTRODUCTION

Solvent sublation is a technique in which the material raised to the surface of a solution by flotation is collected and prevented from redispersing into the bulk phase. This is achieved by spreading a thin layer of an immiscible organic solvent on the surface of the solution which causes the floated material to dissolve or to become suspended. Sebba (*1*) introduced solvent sublation as an adjunct to ion flotation but it can be conveniently used with other adsorptive bubble separation methods. The few papers that have appeared in this field are reviewed by Karger, Pinfold, and Palmer (*2*) who also propose a mechanism for

---

* Present address: Department of Civil and Municipal Engineering, University College London, Gower Street, London WC1, England.

the process. The conclusions were based not only on the investigations described in that paper but also on those by Spargo and Pinfold (*3*), and on the results to be described below.

As bubbles pass through a solution containing surfactant ions (collector) and surface-inactive ions of opposite charge (colligend), the two species adhere to each other by coulombic attraction and are attached to the bubbles by the surface activity of the collector. The collector–colligend product, or sublate, is then lifted to the surface of the solution and either forms a foam or is retained in an immiscible organic layer, if such a phase is present.

It is known that a greater amount of sublate can be removed from the solution by solvent sublation than by solvent extraction, and that this amount, when using the former technique, is independent of the volume of the immiscible phase present. As long as flotation is in progress, therefore, the system as a whole is not in thermodynamic equilibrium and only returns to this state on discontinuing the flow of bubbles. The investigation described below, in which this return to equilibrium was studied, proved helpful in formulating an acceptable mechanism of the process.

Two other aspects of solvent sublation are illustrated by the following results. First, there is evidence to support the contention of Karger, Pinfold, and Palmer (*2*) that flotation is hampered by the small amount of immiscible solvent which leaves the layer on the surface and dissolves in the aqueous phase. Second, the usefulness of solvent sublation, under certain conditions, in retaining floated material and preventing its redispersion into solution is illustrated.

In addition, the investigation described below is the first to be made on a solution containing collector only. In other investigations, interest has centered on the removal of colligends without knowing how the collector behaves under similar conditions.

EXPERIMENTAL

Materials

Hexadecyltrimethylammonium chloride (HTMAC) was obtained from Armour & Co., Illinois, and was used without further purification. The extent of flotation was followed using a radioactive HTMAC label, obtained from The Radiochemical Centre, Amersham, England.

Apparatus

The flotation cell used has been described elsewhere (*4*). It was of 2 liter capacity and contained a fine porosity frit, the average pore size of which was 10^{-5} *M*. Nitrogen gas was used for the flotations.

Procedure

A volume of 1500 ml of the solution to be floated was prepared by adding the requisite amounts of collector, radioactive label, and salt, together with 10 ml of ethanol to reduce the sizes of the gas bubbles. The solution was poured into the cell, about 5 ml was withdrawn through the sampling tap, and 1 ml of this sample was weighed into a container to be used for scintillation counting. A volume of 20.0 ml of 2-octanol was spread on the surface of the solution, and nitrogen was passed into the cell at 2 or 5 l/hr. More samples were taken at predetermined times after the commencement of the run, which lasted 50 to 60 min. The samples were prepared (*4*) and counted on a scintillation spectrometer, and the percentage recoveries determined by proportion-

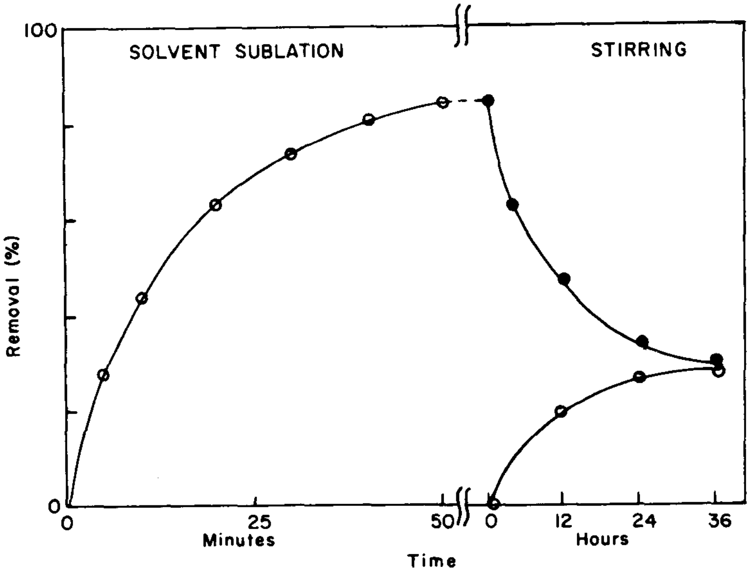

FIG. 1. The removal of HTMAC from 10^{-5} *M* solutions by solvent sublation or stirring.

ately comparing the count rate of all samples with that of the initial sample taken before flotation commenced. The flotation curve was then obtained by plotting percentage recovery against time.

RESULTS AND DISCUSSION

To demonstrate that the organic and aqueous phases are not at equilibrium during solvent sublation, flotation was continued in a number of systems until the percentage removal had attained a high value. The passage of gas was then discontinued and a stirrer was inserted into the aqueous phase. It was rotated at a speed such that the stirring was efficient without unduly perturbing the octanol–water interface and causing emulsification. Sampling of the aqueous solution was continued and showed that collector gradually returned from the organic layer until its concentration in the aqueous phase became constant. In other experiments, no bubbling was performed but the solution was stirred from the commencement. The percentage removals of HTMAC then increased with time over a period of 12–36 hr and attained the same final equilibrium values, within 2%, as had been obtained above. This behavior for 10^{-5} *M* HTMAC solutions in the presence of 10^{-3} *M* sodium chloride is shown in Fig. 1. [It has been shown (*4*) that the presence of an added salt is essential to the flotation of a collector. If the ionic strength is not increased by such additions, very poor recoveries are achieved.]

It was found that the rate of flotation and the extent of removal of

TABLE 1

Removal of HTMAC into 2-Octanol by Solvent Sublation and Solvent Extraction (Stirring)

Concn of sodium chloride (*M*)	Volume of 2-octanol (ml)	% Removal		K^a
		Solvent sublation	Solvent extraction	
10^{-3}	20	80	34	3.8×10^{-4}
10^{-3}	100	80	70	3.5×10^{-4}
10^{-2}	20	95	84	3.8×10^{-4}

[a] $K = [\mathrm{HTMAC}]_{\mathrm{octanol}}/[\mathrm{HTMA}^+]_{\mathrm{aq}}[\mathrm{Cl}^-]_{\mathrm{aq}}$.

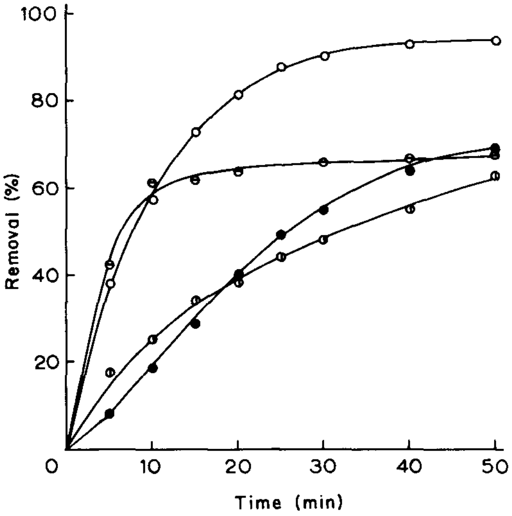

FIG. 2. The removal of HTMAC from 10^{-5} *M* solutions containing sodium chloride. Gas flow-rate: 2 l/hr. Solvent sublation: (○) 10^{-2} *M* NaCl, and (◐) 10^{-3} *M* NaCl. Flotation: (⊖) 10^{-2} *M* NaCl, and (●) 10^{-3} *M* NaCl.

HTMAC into the organic layer were independent of the volume of that layer. This behavior has been found by all investigators in the field and the mechanism proposed by Karger, Pinfold, and Palmer is consistent with it. On the other hand, the ultimate percentage removal of HTMAC at equilibrium must, of course, depend markedly on the volume of the organic phase. Table 1 gives a comparison of the values obtained after 50 min of flotation and after 36 hr of stirring for 10^{-5} *M* HTMAC solutions in the presence of sodium chloride. It is clear how markedly extractions by solvent sublation can be made to exceed equilibrium.

A comparison of flotation and solvent sublation is shown in Figs. 2 and 3. Solutions of 10^{-5} *M* HTMAC in the presence of sodium chloride were subjected to either flotation or solvent sublation at gas flow-rates of 2 and 5 l/hr. For solutions 10^{-3} *M* with respect to sodium chloride, it can be seen that there is little difference in the rates of flotation and solvent sublation at 2 l/hr but that at higher gas flow-rates flotation is clearly the more rapid process. In the presence of 10^{-2} *M* sodium chloride, however, there is little variation in behavior between the two processes at different flow rates.

Table 2 shows the first-order rate constants for both processes under some of the above conditions, using a method described by Sheiham

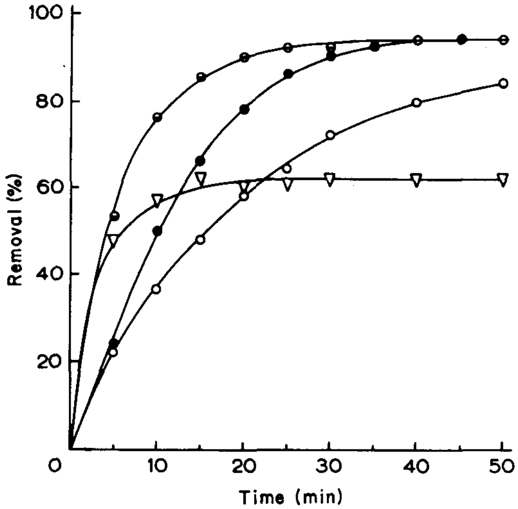

Fig. 3. The removal of HTMAC from 10^{-5} *M* solutions containing sodium chloride. Gas flow-rate: 5 l/hr. Solvent sublation: (⊖) 10^{-2} *M* NaCl, and (○) 10^{-3} *M* NaCl. Flotation: (▽) 10^{-2} *M* NaCl, and (●) 10^{-3} *M* NaCl.

and Pinfold (*4*). (The results for flotations in the presence of 10^{-2} *M* sodium chloride have been omitted, as drainage from the foams was appreciable under these conditions. The kinetics of this redispersive process are ill-defined, and when it occurs to an appreciable extent, the rates calculated for flotation become suspect.) From the results it is clear that solvent sublation is slower than flotation. Also the ratio of the rate constants (β) at gas flow-rates of 5 and 2 l/hr are appreciably lower than those that have been found for flotations (*4*), and also below the value of 2.1 which is the ratio of the total bubble surface areas, determined photographically, at the two flow rates.

TABLE 2

Rate Constants for Flotations and Solvent Sublations of 10^{-5} *M* HTMAC

Process	Concn of NaCl (*M*)	Rate constant $(\text{min})^{-1}$		Ratio of rate constants β
		2 l/hr	5 l/hr	
Flotation	10^{-3}	0.031	0.099	3.2
Solvent sublation	10^{-3}	0.025	0.046	1.8
	10^{-2}	0.10	0.14	1.4

These results are in keeping with the suggestion of Karger, Pinfold, and Palmer (*2*) that flotations are slowed down by solution in the aqueous phase of the organic substance used on the surface of the solution for solvent sublation. Octanol, for example, is surface active and will compete with collector ions for positions on the surfaces of the bubbles. In the initial stages of flotation this interference will be insignificant but as greater amounts of the organic substance dissolve, aided by the turbulence in the water, the effect increases. Further, it will be more marked the higher the gas flow-rate; the turbulence and the rate at which 2-octanol dissolves in water, for example, will be greater at 5 l/hr than at 2 l/hr.

Such interference by 2-octanol probably accounts for the slower removal of colligend which occurs when the organic phase is present. It also explains the low values of β, which arise because the interference is greater at the higher flow rate and the ratios are consequently lowered.

Although solvent sublation is often slower than flotation in the absence of an organic layer, it may be considerably more useful in that redispersive processes, such as foam drainage, do not occur. Once the sublate has moved into the organic phase, virtually none of it returns to the solution while the passage of bubbles continues. With foams, however, considerable instability may be unavoidable because of the nature of the aqueous solution, and drainage may result in the incomplete removal of colligend.

The effect is shown in Figs. 2 and 3 where removals of HTMAC by solvent sublation approach 100% whereas in the absence of the 2-octanol layer the final recoveries are scarcely better than 60%. This occurs because in the presence of 10^{-2} *M* sodium chloride the foam formed is unstable due to a reduction by the electrolyte of the zeta potentials of the lamellae surfaces in the foam. Repulsions between opposite sides of the lamellae are then reduced, leading to thinning and ultimate collapse of the structure. With 10^{-3} *M* sodium chloride solutions the ionic strength is lower, the foam is considerably more stable, and the use of solvent sublation is an unnecessary complication. A decision as to whether solvent sublation should be used therefore depends on the stability of the foam that would otherwise be formed.

Acknowledgments

The authors wish to thank Dr Barry L. Karger for his assistance and helpful criticism. In addition, they gratefully acknowledge the financial support of the Atomic Energy Board, Pretoria, South Africa.

REFERENCES

1. F. Sebba, *Ion Flotation*, Elsevier, Amsterdam, 1962.
2. B. L. Karger, T. A. Pinfold, and S. E. Palmer, *Separ. Sci.*, *5*, 603 (1970).
3. P. E. Spargo and T. A. Pinfold, *Separ. Sci.*, *5*, 619 (1970).
4. I. Sheiham and T. A. Pinfold, *Separ. Sci.*, *7*, 25 (1972).

Received by editor May 3, 1971