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Studies in Batch and Continuous Solvent Sublation. IV. Continuous Countercurrent Solvent Sublation and Bubble Fractionation of Hydrophobic Organics from Aqueous Solutions

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Abstract

Experimental results on the solvent sublation of four hydrophobic compounds [pentachlorophenol (PCP), 1,2,4-trichlorobenzene (TCB), 2,3,6-trichloroanisole (TCA), and 2,4,6-trichlorophenol (TCP)] from the aqueous phase to organic solvents are reported. The experiments were conducted with the aqueous and air phases in continuous countercurrent modes and the organic solvent as a stagnant layer. TCB, TCA, and TCP were sublated into mineral oil. PCP at pH 2.9 as neutral molecules were sublated into mineral oil and decyl alcohol while ionic PCP at pH 8.9 were sublated as a complex with hexadecyltrimethyl ammonium bromide into decyl alcohol. The effect of the two organic solvents were compared for neutral PCP sublation from the aqueous phase. The effects of air flow rates, influent feed rates, and the volume of organic solvent were studied. Comparisons were made between the bubble fractionation and solvent sublation of neutral PCP and TCP into mineral oil. The efficiency of sublation was largest for TCB, smallest for TCP, and followed the relative magnitudes of "effective" partition constants for the solutes between the air bubble and aqueous phase.

INTRODUCTION

Adsorptive bubble processes show promise as wastewater treatment processes. Most of these have, however, remained laboratory curiosities. Processes such as ore flotation have enjoyed extensive investigations for the recovery of valuable minerals from their ores. Precipitate and adsorbing colloid flotation have been attempted on pilot-scale equipments as wastewater treatment processes (*1*). These processes, however, involve the pro-

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duction of a large amount of foam. Two processes that do not involve extensive foaming (called "nonfoaming adsorptive bubble techniques") are bubble fractionation and solvent sublation (*2*). Both of these techniques involve utilizing large axial concentration gradients in tall, narrow bubble columns to effect the separation of hydrophobic compounds. In solvent sublation, a floating immiscible organic solvent is used at the top of the aqueous section to extract the material carried by the bubble. Solvent sublation combines the effectiveness of both bubble fractionation/air stripping and solvent extraction, and it has certain advantages over both (*3*). Most of the work to date on solvent sublation has been laboratory-batch-scale tests to identify the mechanisms of solute transport between the organic solvent and aqueous phases. This paper describes some of our experiments on laboratory-scale bubble columns in continuous modes of operation. We believe such tests are important in elucidating the effectiveness of the technique as a practical wastewater treatment process. We chose as our target contaminants in water four chlorinated aromatic compounds, both polar and nonpolar. The compounds were pentachlorophenol (PCP), 1,2,4-trichlorobenzene (TCB), 2,3,6-trichloroanisole (TCA), and 2,4,6-trichlorophenol (TCP) (see Table 1 for properties). TCA and TCP are neutral and moderately hydrophobic, of low aqueous solubilities and vapor pressures, and are considered partly volatile. Hence their removal occurs both inside and on the bubble surface. PCP, on the other hand, is polar, nonvolatile, of very low aqueous solubility and vapor pressure, and removal occurs exclusively on the bubble surface. However, its aqueous solubility and hydrophobicity vary with pH. At low pH values ($<\mathrm{p}K_a$, which is 4.7) it exists as a neutral hydrophobic molecule of extremely low aqueous solubility while above pH values of 4.7 it exists as an anion that is hydrophilic. The removal of anionic PCP can be accomplished by complexing with a cationic surfactant and sublating the ion–surfactant complex

TABLE 1
Properties of Hydrophobic Compounds Used

Property	PCP	TCA	TCB	TCP
Molecular weight	266	298	181	197
Aqueous solubility (mg/L)	14	31	49	800
Vapor pressure (mmHg)	1.95×10^{-5}	0.023	0.40	0.015
Henry's constant, H_c (—)	2.0×10^{-5}	0.0118	0.08	0.0002
Adsorption constant, K_a (cm)	2.0×10^{-4}	3.6×10^{-5}	9.6×10^{-4}	1.6×10^{-5}
Mineral oil–water partition constant, K_{ow}	800	730	1000	—
$(H_c + 3K_a/r)$ for $r = 0.01$ cm	0.06	0.02	0.37	0.005

(*3*). Thus our experiments were designed to study the removal of both neutral molecules and ion–surfactant complexes.

The sublation of nonpolar molecules can be accomplished by using nonpolar solvents, but the removal of polar molecules requires that the solvent be partly polar. In the latter case, the solvent redissolution into the aqueous phase should be kept minimal. Thus, compromise solvents have to be chosen. Hence, the two solvents chosen in this study were mineral oil (nonpolar) and decyl alcohol (polar).

In this paper we first describe the transport mechanisms in solvent sublation. The difference between the sublation of neutral and ion–surfactant complexes is explained with reference to the removal of PCP into decyl alcohol. Continuous countercurrent results on the four hydrophobic compounds are described. Several process variables were studied.

EXPERIMENTAL

Figure 1 is a sketch of the bubble column used for sublation. Complete description of the apparatus is available elsewhere (*3*). Experimental details for both semibatch and continuous operations are also given elsewhere (*4*). In all of the countercurrent experiments except for the ones involving

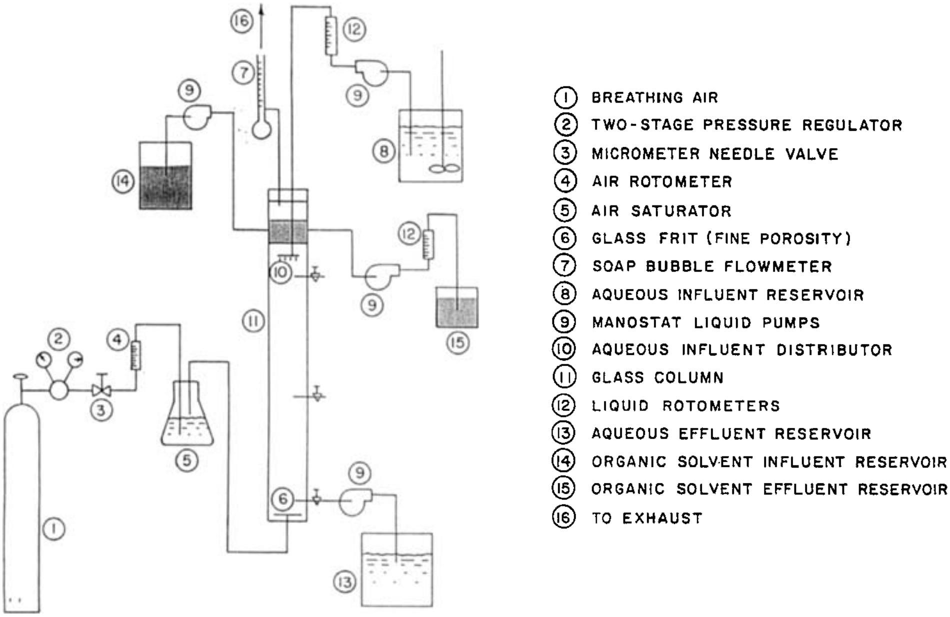

FIG. 1. Sketch of the sublation column used for continuous countercurrent experiments.

feed location changes, the influent was fed at about 8 in. down in the aqueous layer from the aqueous–organic solvent interface.

The pentachlorophenol (PCP), 1,2,4-trichlorobenzene (TCB), 2,3,6-trichloroanisole (TCA), and 2,4,6-trichlorophenol (TCP) used were supplied by Aldrich Chemicals. Mineral oil was obtained from Fisher Scientific, and decyl alcohol was supplied by Matheson, Coleman and Bell. Hexadecyltrimethyl ammonium bromide (HTMAB) was supplied by Kodak Chemicals. Saturated aqueous solutions of the compounds were prepared by overnight stirring and subsequently filtering to remove any particulate materials.

The aqueous samples (both influent and effluent) obtained during the experiments were analyzed for the hydrophobic compounds as follows.

PCP samples in the aqueous phase (both neutral and ion–surfactant complexes) were acidified using 6 *N* sulfuric acid and analyzed as neutral species by measuring the UV absorbance at its absorbance maximum of 214 nm on a Hewlett-Packard 8452A UV-Visible Diode Array Spectrophotometer. TCP samples were analyzed similarly after acidification, and absorbance at 204 nm was monitored. Concentrations were obtained by comparison with the absorbance of calibration standards in methanol.

TCA and TCB analyses were made by first extracting the aqueous samples into hexane (4 mL sample extracted with 1 mL hexane) and subsequent injection of 2 μL of the hexane sample into a Hewlett-Packard 5890A Gas Chromatograph equipped with an electron capture detector. The GC columns used was an HP 530μ series capillary column 12 m long and of 0.01 cm diameter, and it was coated with crosslinked methyl silicone (OV-1). The temperatures of oven, detector, and injector were 150, 300, and 250°C respectively. 99.9% prepurified nitrogen was used as the carrier gas. Hamilton 701N 10 μL syringes were used for sample injection. The peaks were stored and integrated on an HP 3392A Computing Integrator.

RESULTS AND DISCUSSION

Solvent sublation combines the effectiveness of solvent extraction, bubble fractionation, and air stripping in bubble columns, but with added advantages over all three operations. It is superior to air stripping since it is also capable of removing nonvolatile materials as in bubble fractionation (*6*). As compared to solvent extraction, sublation offers two advantages—first, the degree of redissolution of solvent in the aqueous phase is minimized, and second, because it is a rate-controlled process (unlike solvent extraction, which is an equilibrium controlled operation), the solvent extraction efficiency can be exceeded under certain conditions (*3, 5*). Figure 2 shows the different mechanisms occurring in extraction, sublation, and air stripping processes. In order to utilize the advantages of sublation, one

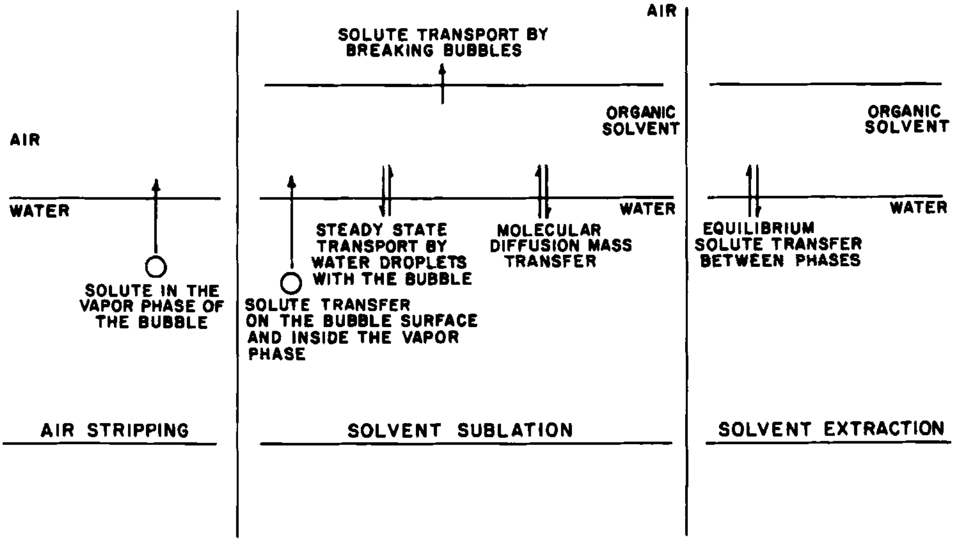

FIG. 2. Mechanisms of solute transport in air stripping, solvent sublation, and solvent extraction.

should first understand the various transport mechanisms between the aqueous and organic solvent phases in sublation.

In the first of a series of papers we have published (*3*), we described the mechanism of sublation in detail and proposed a mathematical model to describe it. Basically, there are two different and simultaneous transport mechanisms in solvent sublation: 1) the transport of materials by the air bubbles (both inside as vapor and as surface adsorbed on the air bubbles), and 2) a molecular diffusion process dependent on the solute concentration gradient between the organic solvent and aqueous phases. The latter is characterized by a mass transfer coefficient, k_1, which depends on the degree of turbulence at the solvent–water interface and the organic solvent–water partition constant of the solute, K_{ow}. The former mechanism is dependent on the air flow rate (Q_a), the bubble radius (r), the mass transfer coefficient of the solute to the bubble in the aqueous phase (k_w), and the combination of Henry's constant (H_c) and adsorption constant for the solute at the air–water interface of the bubble (K_a) for the solute, i.e., ($H_c + 3K_a/r$). The term ($H_c + 3K_a/r$) can be considered an "effective" partition constant for the solute between the air bubble and the aqueous phase; the larger this value, the higher the capacity of the hydrophobic compound to be associated with the air bubble. If k_1 and K_{ow} are very large, then the maximum efficiency one can obtain in sublation is that of solvent extraction, but with the advantage that the residual solvent in the aqueous phase is smaller in sublation. However, under conditions when k_l and K_{ow} are small, one can, by increasing Q_a and decreasing r, achieve sublation efficiencies larger than that achievable by solvent extraction. This was proved experimentally and theoretically by us earlier (*3*). We showed that for a K_{ow} value of 100 and k_l of 3 cm/min at an air flow rate of 1.8 mL/min, the extraction efficiency for a typical compound was only 0.62. Upon increasing the air flow rate, the steady-state removal also increased. This increased further with decreasing bubble radius. Thus it showed that extraction efficiency can be exceeded by sublation under appropriate conditions. We also showed that upon stopping the air flow rate and allowing the phases to equilibrate, the removal efficiency should return to that of extraction, which was also shown by our model (*3*). This effect was shown to be true experimentally for the solvent sublation of the PCP + HTMAB complex into decyl alcohol (*3*). We also observed from mathematical simulations of our semibatch experimental results that neutral PCP sublation showed no particular improvement over extraction in the amount of material removed at steady state except that the rate of sublation was faster at higher air flow rates and obtained larger k_l values for neutral PCP sublation into decyl alcohol as well as mineral oil. On the other hand, the simulation of sublation of the PCP + HTMAB complex into decyl alcohol showed small k_l values. The dependence of sublation efficiency on the organic solvent volume was observed to be important only when k_l was large (*4*). If k_l is small, then solvent sublation has the added advantage over extraction in that the organic solvent volume is unimportant in solvent sublation.

We next describe the results of our experiments on the countercurrent solvent sublation of the four hydrophobic compounds described in the Experimental section. There are various process configurations in which solvent sublation can be carried out (*4*). The present experiments were carried out with the air and aqueous phases in countercurrent flow and a stagnant organic solvent layer. Some of the results are presented as efficiency versus time to display both the rate of approach to steady state and the ultimate steady-state efficiency.

The first series of experiments were conducted on the removal of PCP anions as the PCP + HTMAB complex at pH 8.9 into decyl alcohol from aqueous solutions presaturated with decyl alcohol. Figure 3 shows the result. First if all, the rate of removal was fast compared to neutral PCP removal (discussed later), and removal efficiency R approached 1.0 in about 2 h at an air flow rate, Q_a, of 22 mL/min and an influent feed rate, Q_w, of 2.5 mL/min. The value of R, however, fell to 0.88 at Q_w = 5.0 mL/min. Thus it was clear that the removal was a sensitive function of the

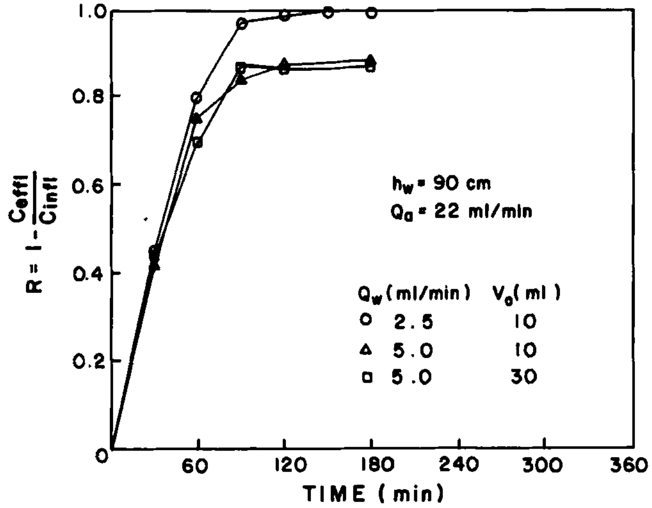

FIG. 3. Continuous countercurrent solvent sublation of PCP + HTMAB complex into decyl alcohol.

ratio Q_a/Q_w. Increased liquid flow rate not only leads to increased axial dispersion in the column, it also decreases the bubble–water contact time in the aqueous phase, both of which tend to decrease the removal rate and steady-state efficiency. The second and more significant observation was that in this case the steady-state removal was independent of the decyl alcohol volume. This is in agreement with our previous results on the semibatch scale (*3*) and reinforced our conclusion (*4*) that in the case of PCP + HTMAB removal into decyl alcohol, the value of k_1 is nearly negligible. Combined with the fact that K_{ow} was only about 100, this clearly indicated that air flow rate was the only important factor in the solvent sublation of the PCP + HTMAB complex. This means that a very small volume of decyl alcohol can be used to decontaminate a very large aqueous volume; this can continue until the maximum solubility of the complex in decyl alcohol is reached, at which point the solvent will have to be replaced.

As mentioned in the Introduction, both bubble fractionation and solvent sublation utilize the large axial concentration gradients in the column for effective separation of surface-active compounds. In bubble fractionation the enriched aqueous section has to be constantly removed to maintain the concentration gradient. In spite of this, the extent of overall removal in bubble fractionation is limited by the aqueous phase dispersion coefficient (*9*). In solvent sublation, on the other hand, the presence of the organic solvent helps capture the material brought to the aqueous surface by the bubble and limits the extent of backmixing, thus maintaining a large axial concentration gradient. In order to show this, we made direct comparisons between the two techniques for neutral PCP removal into mineral oil. In bubble fractionation the influent was fed either halfway up the column or 6 in. from the top of the aqueous section at a flow rate of 6 mL/min; the overflow at the top was 3 mL/min while the effluent rate from the bottom was also 3 mL/min. The sublation runs were made with the influent feed 8 in. from the solvent–water interface at a flow rate of 6 mL/min and the effluent from the bottom at 6 mL/min. The air flow rates were varied from 0.5 to 7 mL/s (30 to 420 mL/min) in both cases, and the steady-state efficiencies obtained in about 2 h operation are plotted in Fig. 4. The distinctly larger removals in sublation as compared to bubble fractionation are seen from Fig. 4. We also noticed that the influent feed location, whether it was 6 in. from the top or halfway up the aqueous section, had little effect on bubble fractionation removal. This seems to be in agreement with some of the results of Wang and coworkers (*10*). The next series of experiments we performed were on the removal of neutral PCP a pH 2.9 by sublation into two organic solvents—decyl alcohol and mineral oil. Both of these solvents are capable of extracting neutral PCP and have partition coefficients for PCP of 5300 (decyl alcohol–water) and 800 (mineral oil–water). However, decyl alcohol, which is partly polar, has a larger aqueous solubility than mineral oil; thus, decyl alcohol has the potential to change

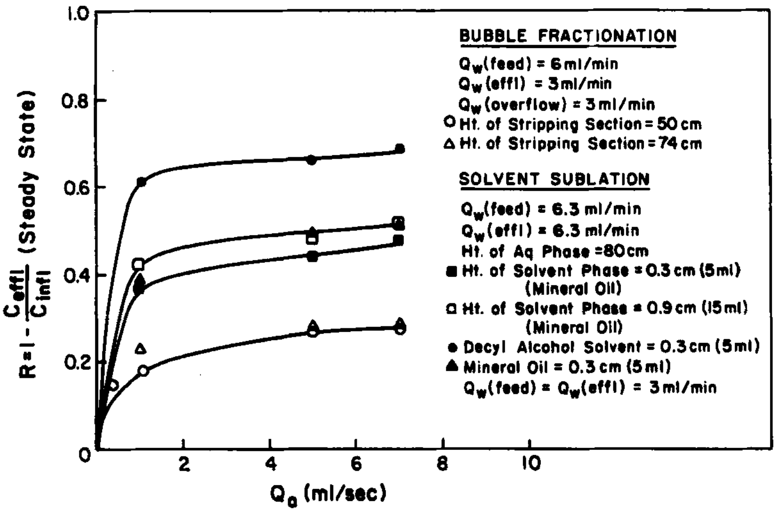

FIG. 4. Steady-state efficiencies of solvent sublation and bubble fractionation of PCP at pH 2.9 from the aqueous phase.

both the bubble characteristics and the aqueous solubility (hydrophobicity) of PCP. We had shown earlier that even when the aqueous phase was saturated with decyl alcohol, the aqueous solubility (hydrophobicity) of PCP was not significantly altered (7). However, because of the reduction of surface tension of water in the presence of even traces of decyl alcohol, the bubble radius decreased and, potentially, a larger surface area would be available for sublation. To distinguish between these effects, two experiments were conducted, one in which the aqueous phase containing PCP was presaturated with decyl alcohol. The results are shown in Fig. 5. They show that the steady-state removal and the rate of sublation of PCP were distinctly higher when the aqueous phase was *not* presaturated with decyl alcohol. It appears, therefore, that decyl alcohol competes for adsorption sites with PCP on the air bubbles when the aqueous phase is presaturated. Under unsaturated conditions in the aqueous phase, this competition is avoided and the constant upward flow of air bubbles tends to carry any residual decyl alcohol dissolved in the aqueous phase during sublation. It also appears that reduced bubble sizes in the presence of decyl alcohol does not appear to lead to any increase in the sublation efficiency, possibly due to the fact that the increased surface area available for adsorption on air bubbles is overwhelmed by the severe competition for adsorption sites.

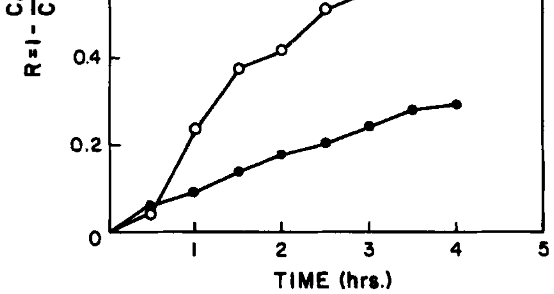

FIG. 5. Effect of presaturation of the aqueous phase with decyl alcohol upon the countercurrent solvent sublation of PCP at pH 2.9 into decyl alcohol.

A comparison of sublation of PCP into the two organic solvents was made under conditions when the aqueous phase was *not* presaturated with the organic solvents. These are also shown in Fig. 4. The liquid flow rate and the organic solvent volumes were kept constant at 6.3 mL/min and 5 mL, respectively. Air flow rates varied from 1 to 7 mL/s (60 to 420 mL/min). The steady-state sublation efficiency was found to be air-flow-rate dependent up to a certain value, beyond which no improvement was noticed. This is clearly as a result of larger bubble radii and larger axial dispersion constants at higher air flow rates, both of which are detrimental to sublation as well as bubble fractionation (*1*, *4*). The steady-state removal was distinctly higher for decyl alcohol than for mineral oil as solvent, as was observed for the semibatch system as well (*3*, *4*). This agreed with our earlier observation (*3*) that the sublation of neutral PCP into either of two solvents was significantly dependent on the molecular diffusion mass transfer coefficient (k_1) and K_{ow} as well as the air flow rate, as was observed in our earlier semibatch results (*3*, *4*). This was reinforced by our results of the solvent volume dependence (for mineral oil) on the steady-state removal of PCP as shown in Fig. 4, in agreement with the theoretical predictions (*3*). The solvent sublation of neutral PCP into mineral oil at different air flow rates, as shown in Fig. 4, indicated that the steady-state removal at a constant Q_a decreased with increasing Q_w. In other words, as in any other gas–liquid contacting device, the steady-state removal increased with the ratio Q_a/Q_w. In about 2 to 3 hours of operation the system reached steady state in all these cases, which is not uncommon for these nonfoaming adsubble processes as was noted by others in bubble fractionation experiments (*8*).

Figure 6 gives the results of countercurrent sublation of TCA into mineral oil. The mineral oil volume was 50 mL with a total aqueous height of 94 cm (37 in.). The air flow rate was maintained at 1.2 mL/s (72 mL/min), and two different influent feed rates, 15 and 39 mL/min, were used. The steady-state removal decreased from 0.44 to 0.35 with increased feed rate. Figure 6 gives similar results for sublation of TCB into mineral oil of volume 85 mL and a total aqueous height of 90 cm. Here again, air flow rate was maintained at 1.2 mL/s (72 mL/min), and three influent feed rates of 9, 48, and 72 mL/min were used. The results for TCB were not as predictable as the other two, especially at high influent feed rates. However, one thing was clear, and that was the increased removal of TCB as compared to other compounds.

Figure 7 gives the steady-state removal efficiencies by sublation and bubble fractionation for TCP into mineral oil as solvent. The vastly improved performance of sublation is clearly evident.

A comparison can be made of the sublation efficiencies for all four compounds (Figs. 4, 6, and 7) even though in the case of TCA and TCB

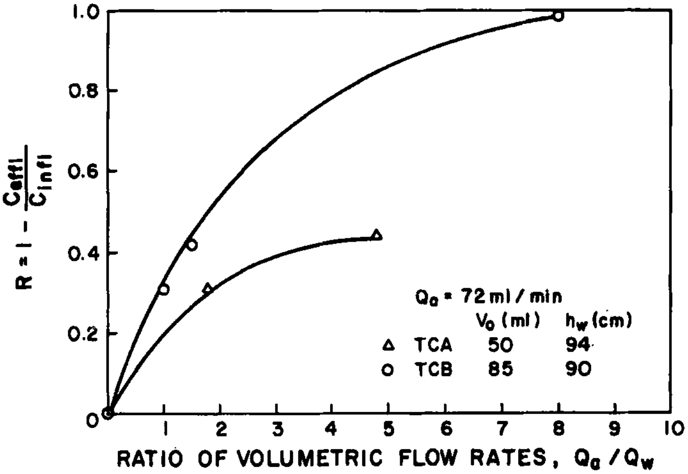

FIG. 6. Countercurrent solvent sublation of TCA and TCB into mineral oil. Effect of influent feed rate.

larger mineral oil volumes were used than for the sublation of PCP and TCP. Also in the case of TCA and TCB sublation, the air flow rate was maintained at 1.2 mL/s (72 mL/min) and the influent feed rate was varied, while for PCP and TCP sublation the influent feed rate was kept constant and the air flow rate was varied. One can, however, compare the results at one constant air flow rate for which values are available, i.e., 1.2

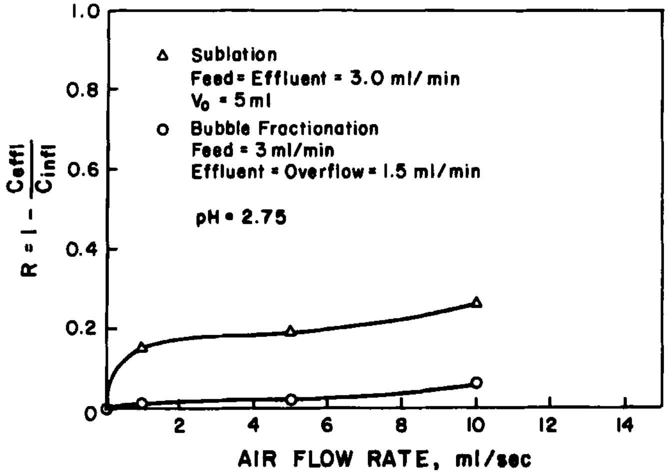

FIG. 7. Countercurrent solvent sublation and bubble fractionation of TCP into mineral oil.

mL/s (72 mL/min) in Figs. 4, 6, and 7, although the influent feed rates are not exactly similar in these cases. The removal is largest for TCB and smallest for TCP, in accordance with the "effective" partition constants, $(H_c + 3K_a/r)$, as given in Table 1. For compounds that have small H_c values, large K_a and small r values will guarantee large removal efficiencies (e.g., TCA, PCP and TCP). Compounds with low K_a values but large H_c values will also show large sublation efficiencies (e.g., TCB). It is likely that highly hydrophobic solutes, if present in large concentrations in the aqueous phase sufficient enough to decrease the surface tension of water, can lead to smaller air bubbles and a larger surface area. This can also contribute to the increased removal of highly hydrophobic compounds. The indication for this is the slight increase in gas-phase holdup in the column in the presence of some of these compounds, as seen in Fig. 8. This effect should be superimposed on the effect of increased "effective" partition constant to give the overall removal efficiencies in sublation.

CONCLUSIONS

Solvent sublation in the continuous countercurrent mode appears to be a feasible method of removing both neutral hydrophobic species and ion–surfactant complexes that are hydrophobic. The process is limited by the rate of attainment of steady state, and therefore the ratio of the air flow rate to the influent feed rate. The organic solvent volume effects the steady-state removal and the rate of sublation only when the molecular diffusion

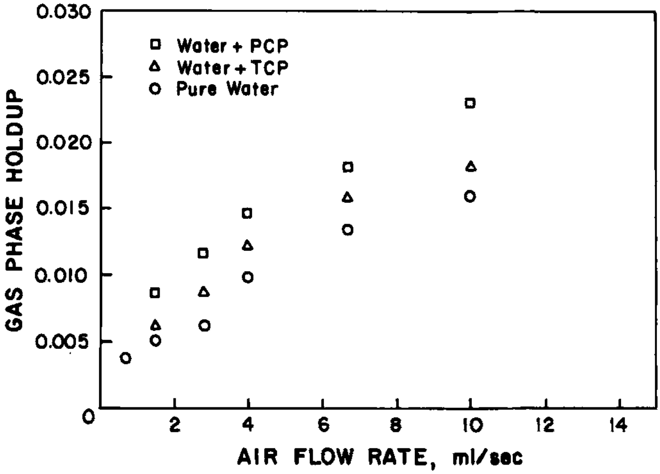

FIG. 8. Gas-phase holdup in the bubble column in the presence of PCP and TCP in the aqueous phase.

mass transfer coefficient of solutes between the aqueous and organic solvent phases is significant. In the experiments reported, only the PCP + HTMAB complex sublation into decyl alcohol is independent of the solvent volume. The type of organic solvent used has a distinct effect on the sublation efficiency. Feed location does not adversely effect the steady-state removal of neutral PCP into mineral oil. The steady-state sublation efficiency (both theoretical and experimental) of neutral hydrophobic compounds into a common organic solvent (mineral oil) vary in accordance with the "effective" partition constant for the solute between the air bubble and the aqueous phase.

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