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

Studies in Batch and Continuous Solvent Sublation. I. A Complete Model and Mechanisms of Sublation of Neutral and Ionic Species from Aqueous Solution

K. T. Valsaraj[a]; L. J. Thibodeaux[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING AND HAZARDOUS, WASTE RESEARCH CENTER LOUISIANA STATE UNIVERSITY BATON ROUGE, LOUISIANA

To cite this Article Valsaraj, K. T. and Thibodeaux, L. J.(1991) 'Studies in Batch and Continuous Solvent Sublation. I. A Complete Model and Mechanisms of Sublation of Neutral and Ionic Species from Aqueous Solution', Separation Science and Technology, 26: 1, 37 — 58

To link to this Article: DOI: 10.1080/01496399108050455

URL: http://dx.doi.org/10.1080/01496399108050455

SEPARATION SCIENCE AND TECHNOLOGY, 26(1), pp. 37–58, 1991

Studies in Batch and Continuous Solvent Sublation. I. A Complete Model and Mechanisms of Sublation of Neutral and Ionic Species from Aqueous Solution

K. T. VALSARAJ* and L. J. THIBODEAUX
DEPARTMENT OF CHEMICAL ENGINEERING AND HAZARDOUS WASTE
RESEARCH CENTER
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA 70803-7303

Abstract

A complete model incorporating all known transport mechanisms for solutes between aqueous and organic solvent phases in solvent sublation is proposed. The predictions from the model with respect to the different transport mechanisms were substantiated with experiments on the solvent sublation of neutral pentachlorophenol (PCP) molecules (pH = 3.0) and ionic PCP molecules as PCP + hexadecyl trimethyl ammonium bromide complex (pH = 8.9) into different solvents—mineral oil (a nonionic solvent) and decyl alcohol (a partly ionic solvent). Effects of inorganic salts on the sublation of both types of PCP molecules were investigated.

INTRODUCTION

There are a number of techniques collectively referred to as "adsubble" processes that make use of the surface-active nature of compounds at air (bubble)–water interfaces to effect their removal from aqueous phases (*1*, *2*). Solvent sublation is one such process suggested first by Sebba (*3*). It involves the transport of both volatile and nonvolatile surface-active compounds by air bubbles with subsequent deposition (extraction of the material in an immiscible organic solvent floating on top of the aqueous section. Ionic compounds can be complexed with surfactant ions of opposite charge and the surface-active ion–surfactant complex can be levitated by air bubbles. Karger (*4*) has written a review of the technique as far as the removal of ionic compounds was concerned. Subsequent reviews (*5*, *6*) focused on the removal of inherently hydrophobic compounds. Recent

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*To whom correspondence should be addressed.

work has focused mainly on evaluating the efficiency of the process as a tertiary wastewater treatment for hydrophobic organic compounds (*7–12*) of environmental significance. Although models have been proposed by various investigators to describe the process (*6*, *7*, *12*), they describe only the transport of material from the aqueous to solvent phases. However, our past work has shown that reverse mass transfer from the solvent to the aqueous phase should not be ignored (*8*, *10*, *13*). The present models are therefore inadquate and incomplete at describing the sublation process. We have undertaken a detailed work to understand the mechanisms of sublation and to build a complete model of sublation. We choose the solvent sublation of pentachlorophenol (PCP) into two different solvents (mineral oil and decyl alcohol) to study the mechanisms of sublation of both neutral and ionic species. Our previous work (*10*) had shown that PCP is unique in that at pH $< pK_a$ it exists as neutral, naturally hydrophobic compounds that do not require any surfactant to effect the removal. At pH $> pK_a$, PCP exists as hydrophilic ions which can be removed only as ion–surfactant complexes. In this paper we describe a complete model of sublation and also elucidate the differences in the mechanisms of removal of PCP as both neutral and ionic species.

EXPERIMENTAL

Pentachlorophenol (99% pure) was supplied by Aldrich Chemical Company. Its properties are summarized in our earlier work (*10*). The two organic solvents used for sublation were light mineral oil (Fisher Scientific) and decyl alcohol (Mallinckrodt). Mineral oil was used only for the sublation of neutral PCP molecules. Hexadecyl trimethyl ammonium bromide (HTMAB) surfactant was supplied by Kodak Chemicals. Saturated aqueous solutions of PCP were prepared by overnight stirring at room temperature. These solutions were diluted with distilled water to obtain approximately 10 ppm PCP solutions.

Sublation runs were made in an apparatus designed for both semibatch and continuous modes of operation. This is shown in Fig. 1. The glass column was 100 cm tall and had an inner diameter of 2.3 cm with access ports at 2, 50, 85, and 90 cm. Liquids were pumped into the column by using Manostat liquid pumps. A fire porosity glass frit was used to introduce air bubbles into the aqueous phase.

Experiments described in this paper were all done with a stagnant aqueous layer and a stagnant solvent layer while the air was used in a once pass-through mode, and hence the overall operation was semibatch. Aqueous samples were withdrawn from the midport for analysis. It is important that to obtain a representative aqueous phase concentration, one should not sample the aqueous phase near the glass frit or near the

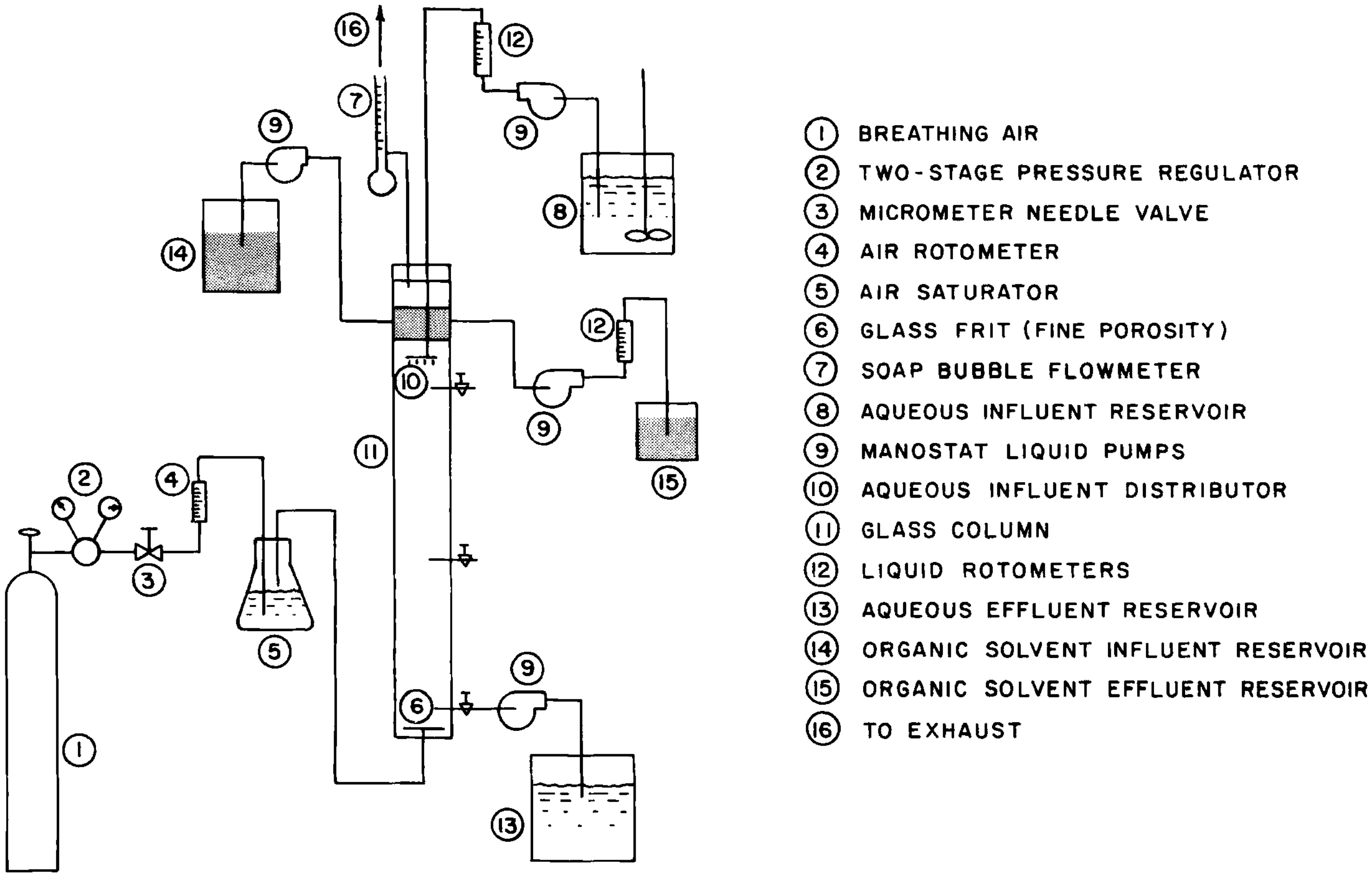

FIG. 1. Equipment for batch and continuous solvent sublation.

aqueous–solvent interface (*4*). Although the analysis of either of the phases would suffice, it is easier to analyze the aqueous phase without substantially changing the volume.

The analysis of PCP was accomplished using a UV/Visible diode array spectrophotometer (Hewlett-Packard Model 8452A) and/or an HPLC using diode array UV detector (Hewlett-Packard Model 1090L). The HPLC column used was a Hypersil ODS column (100 mm long, 4.6 mm i.d.) using 60/40 methanol–water solvent. the samples were analyzed by the UV maximum of 214 nm for PCP. All samples were acidified by using 1 *N* H_2SO_4 before analysis.

RESULTS AND DISCUSSION

Mechanisms and a Complete Model for Sublation

Solute transport between the aqueous and organic solvent phases in sublation can occur in a variety of ways. These are depicted in Fig. 2 along with a comparison with the conventional solvent extraction process. Karger (*4*) first described qualitatively the possible transport pathways in solvent sublation. There are two predominant transport processes: 1) transport within and on the surface of the bubbles, 2) a diffusive transport between the phases driven by a concentration gradient. In the initial stages of sublation the diffusive gradient is exclusively from the aqueous to solvent phase, and as sublation proceeds and the solute concentration builds up in the organic solvent, the reverse transfer to the aqueous phase by molecular (turbulent) diffusion becomes important. Our previous work has shown this to be true (*8*, *10*, *13*). In most cases, unless the physical transport by air bubbles overwhelms the molecular diffusive transport, the decrease in solute concentration in the aqueous phase is distinctly nonlinear. Air bubbles reaching the solvent–water interface do not immediately enter the organic solvent phase since they have to coalesce to form larger bubbles that can then overcome the solvent–water interfacial tension and rise through the organic phase. As they do so, a thin film of water is dragged into the solvent phase and is then returned as water droplets. Solute is carried by the water dragged up; however, the returning water droplets may be depleted in solute concentration. This process of water drag-up and return as droplets reaches an eventual steady state as shown by the dashed lines in Fig. 2. A complete model should include all of these solute transport mechanisms across the interface. Existing models fail to do so and the current work is the first in this regard.

We assume that air bubbles reaching the solvent–water interface are in equilibrium with the aqueous phase. We also assume that axial dispersion in both phases is sufficiently large to make both phases completely mixed.

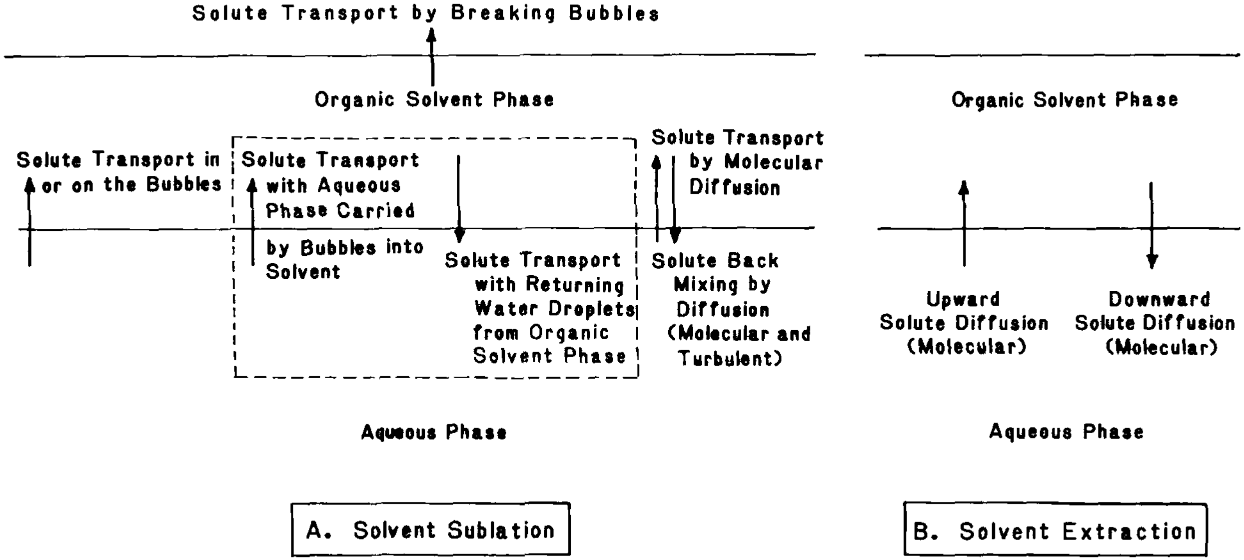

FIG. 2. Solute transport mechanisms in solvent sublation and solvent extraction.

Relaxing this assumption will require that the differential equations be solved numerically (*6*, *7*).

A solute mass balance in the organic solvent layer gives

$$V_o\frac{dC_o}{dt} = Q_a\left[H_c + \frac{3}{a}K_a + \frac{3}{a}d_i\right]C_w + \Pi r_c^2 k_l[C_w - C_o/K_{ow}] - Q_a\left[\frac{3}{a}d_i + H_c\right]\frac{C_o}{K_{ow}} \quad (1)$$

The term $Q_a[H_c + (3/a)K_a]C_w$ gives the transport of solute within and on the surface phase of the bubbles. H_c is the dimensionless Henry's constant for the solute between vapor and aqueous phases. K_a is the linear adsorption constant for the solute between the air–water interface of the air bubbles and the aqueous phase (in centimeters) (see Ref. *9* for details). a is the radius of an air bubble in the solvent phase. The term $Q_a(3/a)d_iC_w$ gives the amount of solute carried up with the water layer of thickness d_i around the bubble. The term $\Pi r_c^2 k_l[C_w - C_o/K_{ow}]$ is the molecular diffusive transport with an aqueous phase controlled mass transfer coefficient k_l (cm/s) across the cross-sectional area Πr_c^2, where r_c is the radius of the column. K_{ow} is the solute partition constant between the organic solvent and aqueous phases. The sign and magnitude of the diffusive transport depend on the values of k_l, C_o, C_w, and K_{ow}. The term $-Q_a(3/a)d_iC_o/K_{ow}$ gives the amount of solute returning with the water droplets from the solvent phase to the aqueous phase, while the last term, $-Q_aH_cC_o/K_{ow}$, is the amount of solute lost to the atmosphere as the material carried within the vapor phase of bubbles at the top of the organic solvent section.

For the semibatch process, an overall solute mass balance across both organic solvent and aqueous phase gives

$$V_wC_{wi} = V_wC_w + V_oC_o \quad (2)$$

where C_{wi} is the initial solute concentration in the aqueous phase (mol/cm^3), and V_w and V_o are, respectively, the aqueous and organic solvent volumes.

We have from Eq. (2):

$$V_o\frac{dC_o}{dt} = -V_w\frac{dC_w}{dt} \quad (3)$$

Along with the initial condition that $C_w = C_{wi}$ at $t = 0$, we get from Eqs. (1)–(3) the following:

$$E = 1 - \frac{C_w}{C_{wi}} = \left(1 - \frac{\beta}{\alpha}\right)(1 - e^{-\alpha t}) \tag{4}$$

where

$$\beta = \frac{1}{K_{ow}V_o}\left[\Pi r_c^2 k_l + Q_a\left(H_c + \frac{3}{a}d_i\right)\right]$$

and

$$\alpha = \frac{Q_a}{V_w}\left(H_c + \frac{3}{a}K_a + \frac{3}{a}d_i\right) + \frac{\Pi r_c^2 k_l}{V_w}\left(1 + \frac{1}{K_{ow}}\frac{V_w}{V_o}\right) + \frac{Q_a}{K_{ow}V_o}\left(H_c + \frac{3}{a}d_i\right)$$

Notice that if $k_l = 0$, we regain the equations originally derived by other investigators who excluded reverse mass transfer from the solvent phase (*6*, *9*). In order to illustrate the effects of various parameters in the model, such as k_l, V_w, V_o, K_{ow}, d_i, Q_a, K_a, and a, we choose PCP as the solute and our experimental column dimensions and conditions.

Figure 3 shows that at low values of air flow rates, the effects of k_l (molecular diffusive transport) on the removal efficiency, E, are more important than at high air flow rates. This is understandable since at high air flow rates the transport of solute by air bubbles vastly overwhelms the molecular diffusive transport.

When molecular diffusive transport (characterized by k_l) becomes important, the organic solvent volume also becomes important. This is shown in Fig. 4. It is clear that when k_l is small, then the removal is independent of the volume of organic solvent. This is characteristic of solvent sublation and is an important advantage over solvent extraction. Sebba (*3*) first suggested that this advantage of solvent sublation results in the fact that a very small amount of organic solvent can be used to decontaminate a large volume of aqueous solution. Under conditions when molecular diffusion is unimportant in comparison to transport on the bubbles, the efficiency is also independent of the solvent–water partition constant of the solute. This is shown in Fig. 5. This aspect of sublation suggests that under such conditions the process is only limited by the maximum solubility of

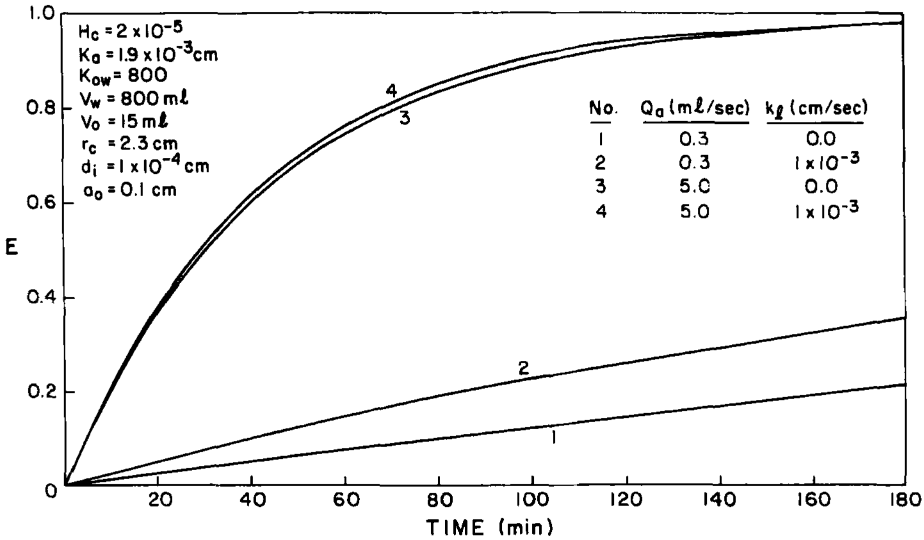

FIG. 3. Effect of molecular diffusion transport coefficient, k_l, on efficiency of solvent sublation at high and low air flow rates.

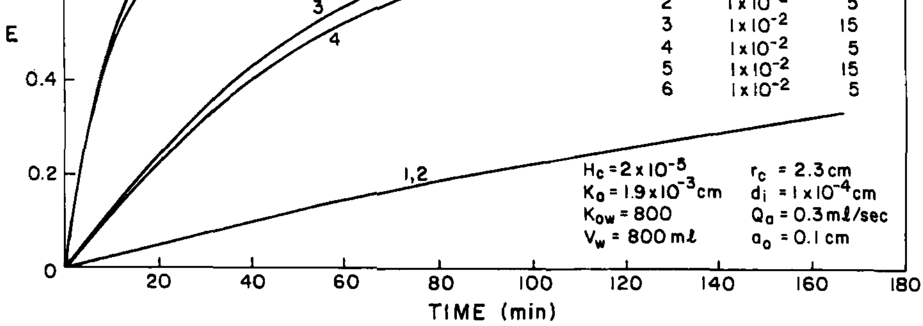

FIG. 4. Effect of molecular diffusion transport coefficient, k_l, and organic solvent volume (phase ratio) on solvent sublation.

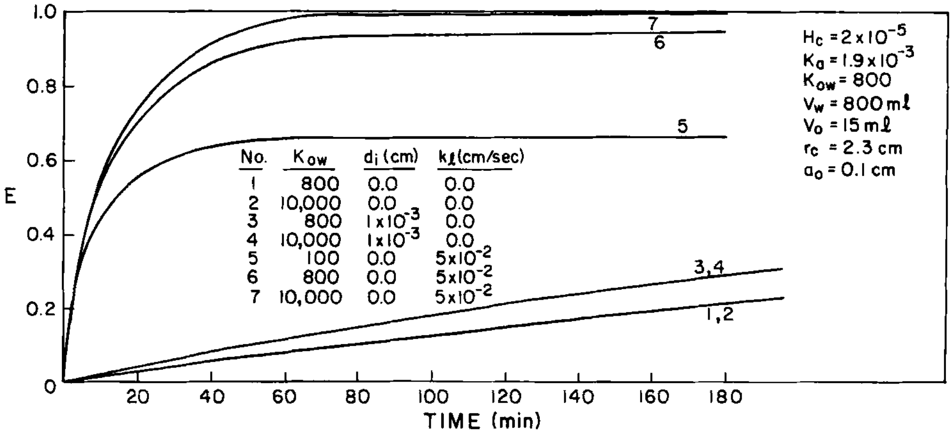

FIG. 5. Effect of solvent–water partition constant of solute at high and low values of k_l and d_i.

the solute in the organic solvent phase. When k_l is very large, Eq. (4) shows that

$$E_{\max} \rightarrow E_{(\text{extraction})} = \frac{K_{ow}(V_o/V_w)}{1 + K_{ow}(V_o/V_w)} \qquad (5)$$

while when $k_l \rightarrow 0$, $E_{\max} \rightarrow 1$.

Figure 6 shows the effect of aqueous phase drag-up by air bubbles into the organic solvent. Since this dragged-up liquid is high in solute concentration while the returning water droplets are depleted of solute, it is not surprising that the overall effect will be to increase the efficiency of removal into the organic layer. Notice that for a bubble of radius 0.1 cm, values of d_i of the order of 10^{-4} cm or so are realistic while the higher values shown in Fig. 6 are unrealistic. It should be mentioned that the small amount of water dragged up by the air bubbles is the only fraction of aqueous phase in real equilibrium with the solvent phase, while the bulk phases are always in disequilibrium. This accounts for the very small mixing of the two phases observed in sublation as compared to solvent extraction (*14*, *15*).

Figure 7 shows the effects of increasing Henry's constant, H_c, and adsorption isotherm parameter, K_a, upon the removal efficiency from the aqueous phase. H_c determines the vapor-phase solute concentration within the bubble while K_a determines that on the surface of the bubble. The model thus considers both volatile and surface-active materials. Increasing H_c and/or K_a increases the amount of material carried by the bubble and hence improves the sublation efficiency. Compounds that are of low vol-

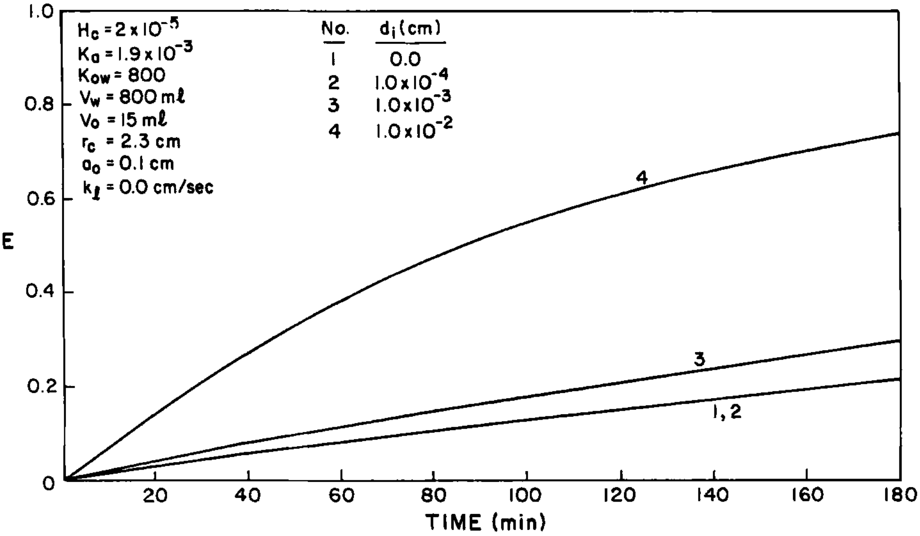

FIG. 6. Effect of aqueous volume dragged into the organic solvent by air bubbles. (Molecular diffusion transport by mixing, k_l assumed zero.)

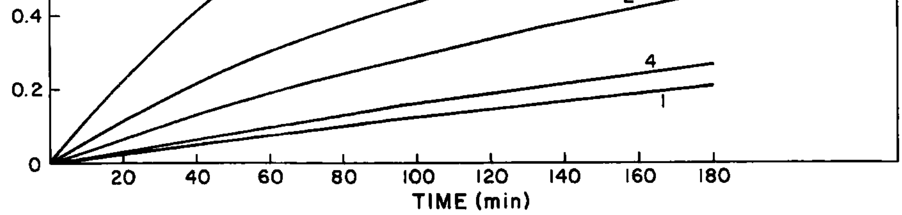

FIG. 7. Effect of increasing Henry's constant, H_c, and adsorption isotherm constant, K_a, on solvent sublation from the aqueous phase.

atility but of high hydrophobic character are traditionally not amenable to conventional air stripping. Solvent sublation, on the other hand, may prove a very viable technique for their removal.

Figure 8 shows that solvent sublation can achieve removal efficiencies higher than that of solvent extraction when higher air flow rates and smaller bubbles are used. High air flow rates increase the flux of air through the column while smaller bubbles generate a larger interfacial area per unit volume of air. Therefore, theoretically, the steady state in solvent sublation is both gas-flow and bubble radii dependent. These two parameters are, however, related in that at higher flow rates, the distribution of bubble radius frequently tends toward larger ones. Therefore, one may not see the expected degree of improvement at higher gas flow rates unless the bubble radius is kept constant. Several of our earlier work showed this to be true (*9*, *10*, *13*). It should be expected that when the bubbles are stopped after sublation has reached a steady state and the aqueous phase is gently stirred, then the equilibrium between the two phases should be reestablished. Such a situation was also analyzed in Fig. 8. The approach to extraction equilibrium conditions after 40 min of sublation is shown as dashed lines in Fig. 8. The analysis is as follows.

A mass balance over the organic solvent section gives

$$V_o \frac{dC_o}{dt'} = -\Pi r_c^2 K_l \left[\frac{C_o}{K_{ow}} - C_w \right] \tag{6}$$

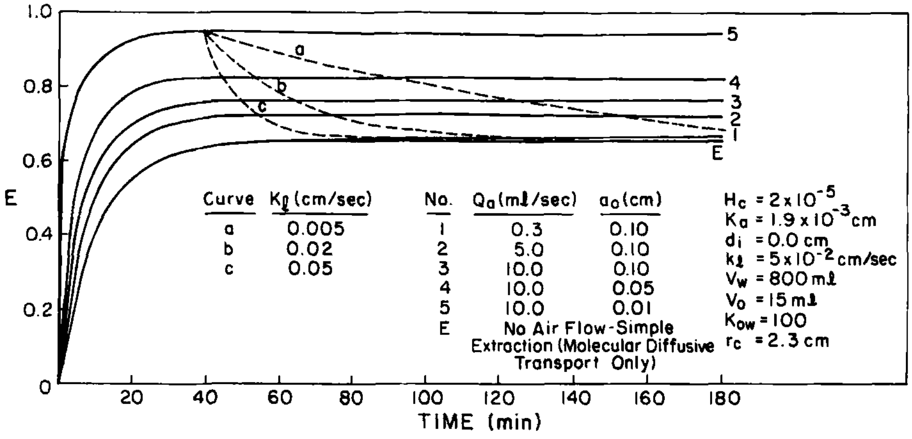

FIG. 8. Improvement of solvent sublation over solvent extraction with high air flow rates and small bubble radius.

where K_l is the overall mass transfer coefficient for solute transfer from the solvent to aqueous phase. It is related to the individual phase mass transfer coefficients as

$$\frac{1}{K_l} = \frac{1}{k_l'} + \frac{K_{ow}}{k_o} \tag{7}$$

where it should be noted that $k_l' \neq k_l$. Depending on the relative magnitudes of k_l' and k_o, the controlling resistance to mass transfer can lie in either of the two phases. Combining Eq. (6) with the overall mass conservation given by Eq. (2) and (3) and using the initial condition that at $t' = 0$, $C_w(t' = 0) = (\beta/\alpha)C_{wi}$, we obtain

$$E = \left(1 - \frac{\beta'}{\alpha'}\right) - \left(\frac{\beta}{\alpha} - \frac{\beta'}{\alpha'}\right)e^{-\alpha' t'} \tag{8}$$

where

$$\frac{\beta'}{\alpha'} = \frac{1}{1 + K_{ow}\dfrac{V_o}{V_w}}$$

β and α are as defined previously.

$$\alpha' = \Pi r_c^2 K_l\left[\frac{1}{V_w} + \frac{1}{K_{ow}V_o}\right]$$

The only adjustable parameter is K_l. Larger K_l tends to accelerate the reestablishment of equilibrium while small K_l values prolong the equilibrium attainment as shown in Fig. 8. It should be remembered that if K_{ow} is very large, then the advantage of sublation can be seen only at low organic solvent volume since increasing V_o will eventually lead to greater than 99% removals even in solvent extraction.

Relationship to Air Stripping/Bubble Fractionation and Effect of pH

The only difference between solvent sublation and conventional air stripping or bubble fractionation (*1*) is the presence of an organic solvent atop the aqueous phase. This should prevent the redistribution of solute at the

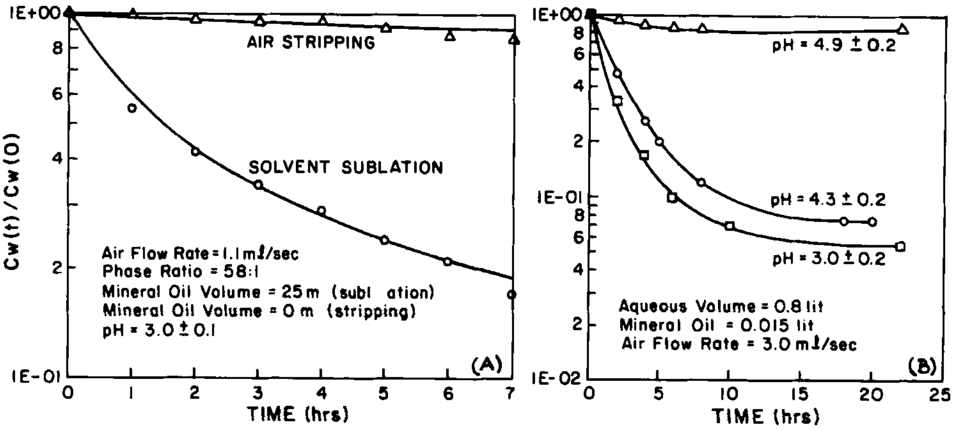

FIG. 9. (A) Comparison of removal of PCP by solvent sublation into mineral oil with air stripping/bubble fractionation. (B) Effect of pH on the solvent sublation of PCP into mineral oil.

top of the aqueous section upon bubble bursting and thus improve the performance of either stripping or fractionation processes. Indeed, such is the case as shown in Figure 9(A) for the solvent sublation of neutral PCP (pH = 3.0) into mineral oil. The vast improvement in sublation as well as the slow approach to a steady state are clear. Figure 9(B) shows that as pH increases, the removal efficiency drops off drastically for PCP molecules. As mentioned earlier, this is due to the high solubility and hydrophilic character of phenolate ions which predominate at pH values greater than the pK_a (= 4.7). Under such conditions, PCP has to be complexed with a surfactant ion (HTMAB) and sublated. Mineral oil proved to be unacceptable under such conditions, and a slightly polar solvent (decyl alcohol) was chosen. Decyl alcohol was chosen over octyl alcohol since the latter has a larger aqueous solubility (580 mg/L) as compared to the former (37 mg/L) (*16*). In order to eliminate the interferences from gradual dissolution of decyl alcohol into the aqueous phase during sublation, all experiments involving decyl alcohol as the solvent were conducted by using water presaturated with decyl alcohol.

The removal of neutral PCP into mineral oil at various gas flow rates is shown in Fig. 10. It is clear that higher gas flow rates do not give correspondingly higher removal efficiencies. This results from the fact that neutral PCP removal into mineral oil is mostly dependent on the molecular diffusive transport between phases (i.e., k_l controlling the sublation), and hence air flow rate has less of an effect. This aspect will become evident in the next section.

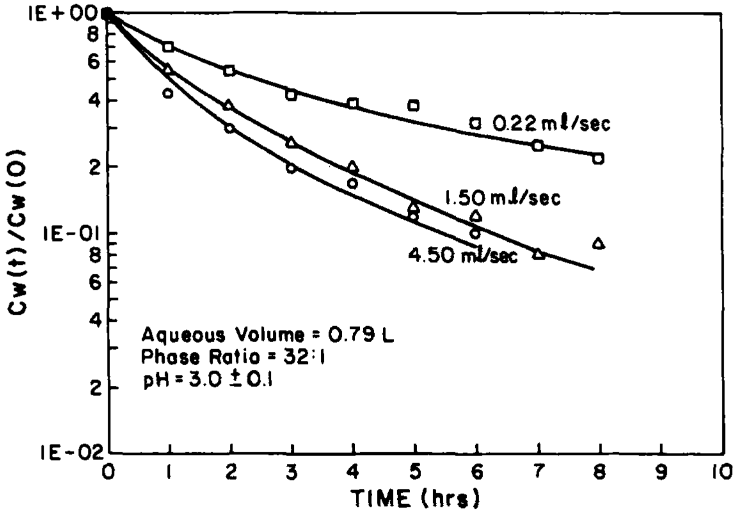

FIG. 10. Effect of air flow rate on the solvent sublation of PCP into mineral oil.

Relationship to Solvent Extraction

Figure 11 shows a comparison between a sublation run for neutral PCP (pH = 3.0) into mineral oil and a similar extraction where the aqueous phase is gently stirred. It is clear that sublation achieves a removal efficiency similar to that of extraction. No improvement was observed. Figure 12, on the other hand, shows the sublation of the complex PCP + HTMAB at pH = 8.9 into decyl alcohol. Clearly the larger-than-equilibrium removal achieved by solvent sublation is evident. In the first cycle of sublation, the *E* value reaches 0.98 at steady state in 40 min whereas extraction with continued stirring achieves an *E* value of 0.65. Upon stopping sublation and stirring the aqueous layer, the equilibrium is reestablished in about 3 days. This clearly shows that the model predictions as to the mechanisms of sublation (Fig. 8) are realistic. Based on the time dependency of the two cases shown in Fig. 12, it is concluded that k_l is very small in this case. Figure 12 also shows that upon restarting sublation, an *E* value close to what was achieved earlier is reached, although not quite the same, possibly due to the loss of some surfactant molecules to the container walls. The behavior of PCP sublation as neutral molecules (Fig. 11) and as ion-surfactant complexes (Fig. 12), along with the general model predictions (Fig. 8), leads us to the conclusion that the molecular diffusive transport driven by a concentration gradient controls the transfer of neutral molecules of PCP, and hence a large k_l value should be expected. However, for ion-surfactant complexes this is not true, and sublation is mainly a result of

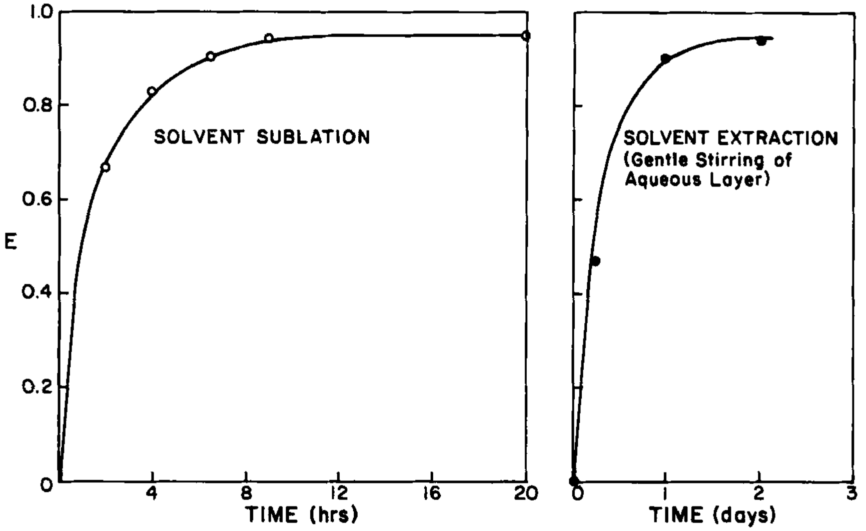

FIG. 11. Solvent sublation and solvent extraction of PCP into mineral oil. Aqueous volume, V_w = 800 mL; mineral oil volume, V_o = 15 mL; 3 × 10^{-5} *M* PCP; pH = 3.0; air flow rate, Q_a = 3 mL/s.

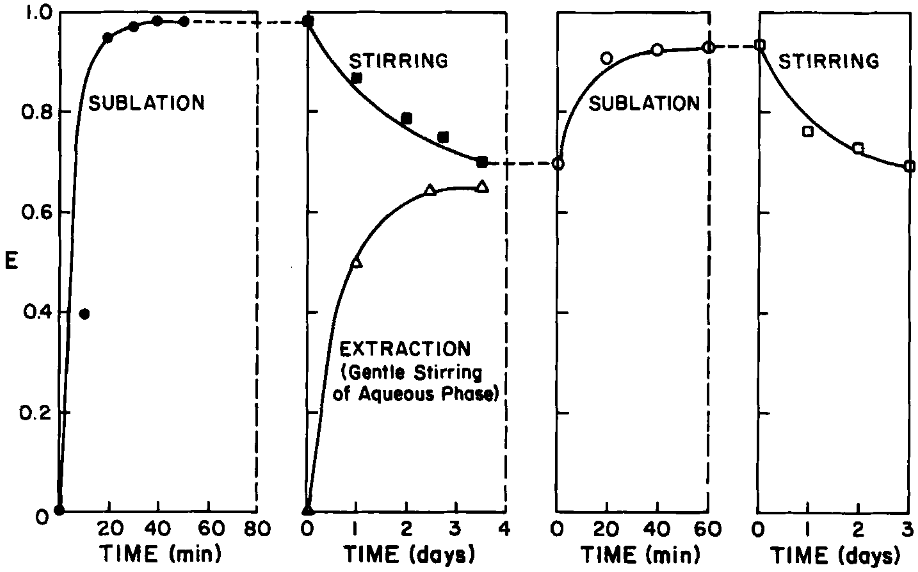

FIG. 12. Improved efficiency of solvent sublation of PCP + HTMAB complex over solvent extraction. V_w = 800 mL; decyl alcohol volume, V_o = 15 mL; 3 × 10^{-5} *M* PCP; 5 × 10^{-5} *M* HTMAB; pH = 8.9; Q_a = 3 mL/s.

bubbles crossing the interface, and k_l should be very small. No backmixing is therefore observed. The work of Karger and coworkers (*17*) and Sheiham and Pinfold (*18*) on the removal of dye–surfactant complexes and surfactant molecules themselves also leads to the same conclusions. Similarly, our previous results on neutral molecules lend credence to the statement regarding the predominance of molecular diffusive transport and backmixing effects (*10*, *13*). In order to show that backmixing effects for neutral PCP sublation into mineral oil resulting from a larger k_l value is significant, two experiments were conducted, one in which the mineral oil was replaced after 4 h (Fig. 13A). The rate of removal was increased as a result. Similar results were observed earlier by us (*8*, *10*, *13*). In another experiment, after sublation reached a steady state in 7 h, the aqueous phase was removed and replaced with clean distilled water. The concentration in the aqueous phase was then seen to increase to the steady value after 7 h. This is shown in Fig. 13(B) where the initial decrease in solute concentration during normal sublation is shown as Curve a, and the increase in aqueous phase concentration after replacement of aqueous phase with uncontaminated distilled water is shown as Curve b.

Having shown that the backmixing due to molecular diffusion is predominant in the sublation of neutral PCP molecules, one should expect from our theoretical model that under such conditions the solvent volume dependence on sublation would be significant. That this is so and that it is not restricted to mineral oil but is significant even for sublation of neutral PCP (pH = 3.0) into decyl alcohol is shown in Fig. 14. On the other hand, the solvent sublation of ionic PCP as PCP + HTMAB complex at pH = 8.9 into decyl alcohol showed no such volume dependence (Fig. 15). In fact, the sublation at two different solvent volumes followed the same experimental curves. It was also seen that increasing the air flow rate had a significant effect on the sublation of the PCP + HTMAB complex as shown in Fig. 15, unlike those of neutral PCP into mineral oil (Fig. 10). Based on these observations, we conclude that the sublation of neutral molecules of PCP is limited by extensive backmixing due to a concentration difference-driven molecular diffusion of solute while such effects are considerably less significant for the PCP + HTMAB complex.

Dependence of Solvent Sublation on Co-Solute Concentration

The sublation of PCP + HTMAB complex is somewhat similar to the sublation of dye–surfactant complexes analyzed earlier by others (*4–6*, *17*). However, we observed that there is an optimum ratio of [PCP] to [HTMAB] that gave the best removal unlike dye–surfactant complexes where excess surfactant concentrations enhanced the removal of the dye

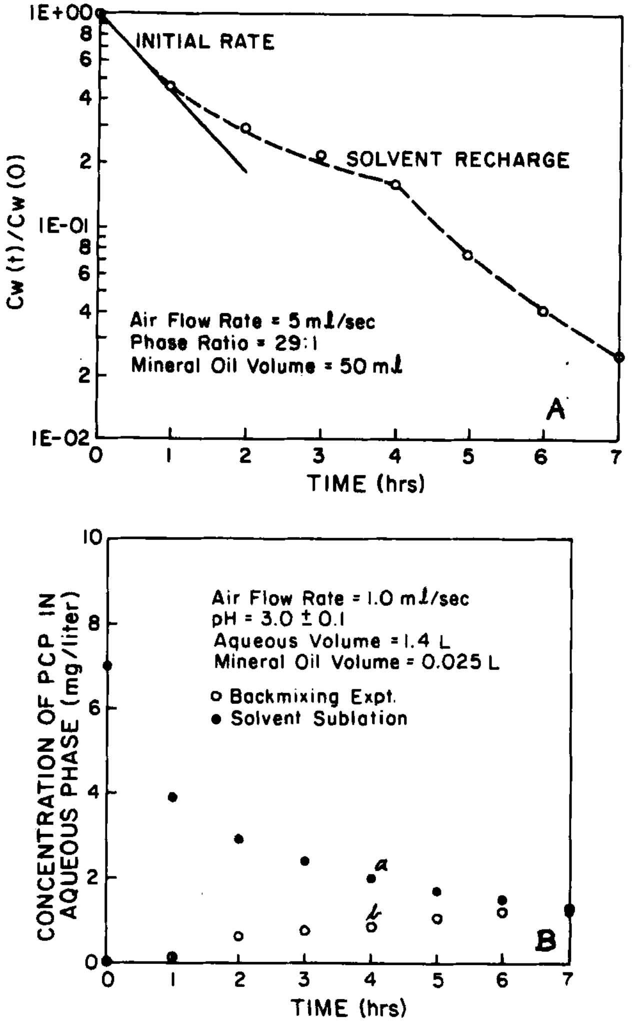

FIG. 13. (A) Effect of solvent recharge on the solvent sublation of PCP into mineral oil at pH = 3.0. (B) Solvent sublation and backmixing of PCP into mineral oil.

(*19*). The removal at low ratios of [HTMAB]/[PCP] was much smaller as was the removal at ratios greater than 1 due to extreme competition for adsorption sites on air bubbles from HTMAB itself. This is shown in Fig. 16(A). It is clear from the figure that a 1:1 ratio works best in obtaining optimum removals. This is another significant advantage of solvent sublation over other processes like foam flotation where excess surfactant is required to create a stable foam (*21*).

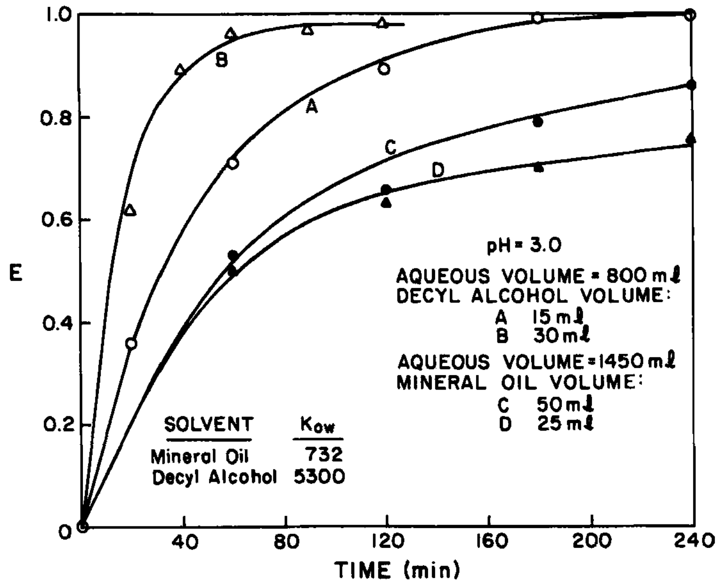

FIG. 14. Effect of solvent volume on the sublation of PCP at pH = 3.0; Q_a = 3.0 mL/s.

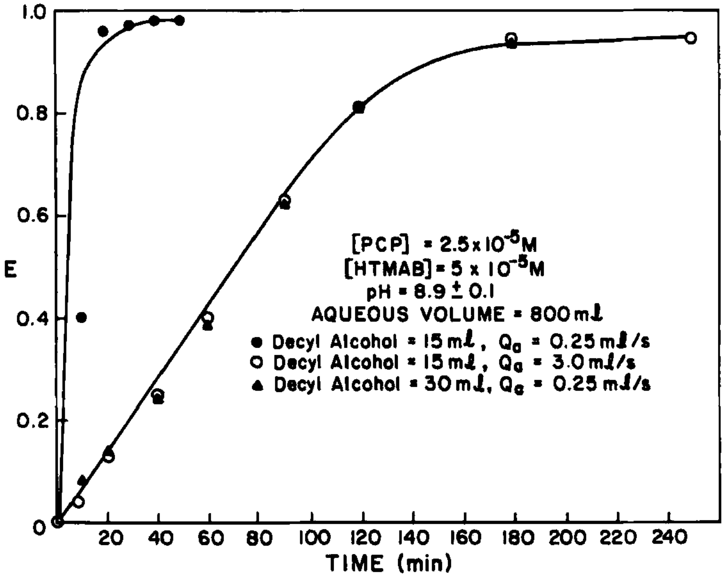

FIG. 15. Removal of PCP + HTMAB complex by solvent sublation into decyl alcohol; effect of solvent volume and air flow rate.

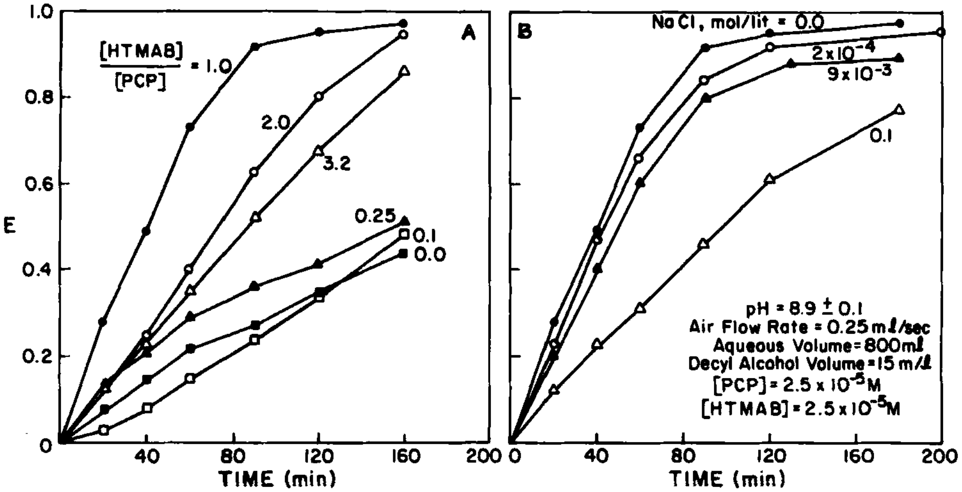

FIG. 16. (A) Effect of HTMAB concentration on the solvent sublation of PCP + HTMAB complex into decyl alcohol. (B) Effect of NaCl concentration on the solvent sublation of PCP + HTMAB complex into decyl alcohol.

The effects of inorganic salts on the sublation of PCP + HTMAB complex at pH = 8.9 are shown in Figs. 16(B) and 17(A) while that for sublation of neutral PCP molecules at pH = 3.0 is shown in Fig. 17(B). Increasing NaCl concentration tends to decrease the rate and steady-state removal of the PCP + HTMAB complex (Fig. 16B); different salts have different effects (Fig. 17A). Similar effects were observed earlier for dye–surfactant complex sublation (*8*, *19*) and were attributed to an ion-pair equilibrium that existed in the aqueous solution between the dye and surfactant molecules. By extending the same arguments to the present situation, we can postulate an equilibrium such as the following to exist in the aqueous solution.

$$\mathrm{HTA^+PhO^-} + \mathrm{Na^+Br^-} \rightleftharpoons \mathrm{Na^+PhO^-} + \mathrm{HTA^+Br^-}$$

Increasing the salt concentration (e.g., NaBr) drive the equilibrium toward a larger concentration of sodium pentachlorophenolate, which is hydrophilic, and less of the PCP–HTMAB complex (i.e., $\mathrm{HTA^+PhO^-}$) exists in the aqueous phase. Hence the rate of removal decreases. Depending on the ability of each salt to effect the equilibrium constant, different degrees of suppression of sublation efficiency results.

On the other hand, the presence of salts tends to increase the removal of neutral PCP molecules into decyl alcohol (Fig. 17B). This is not sur-

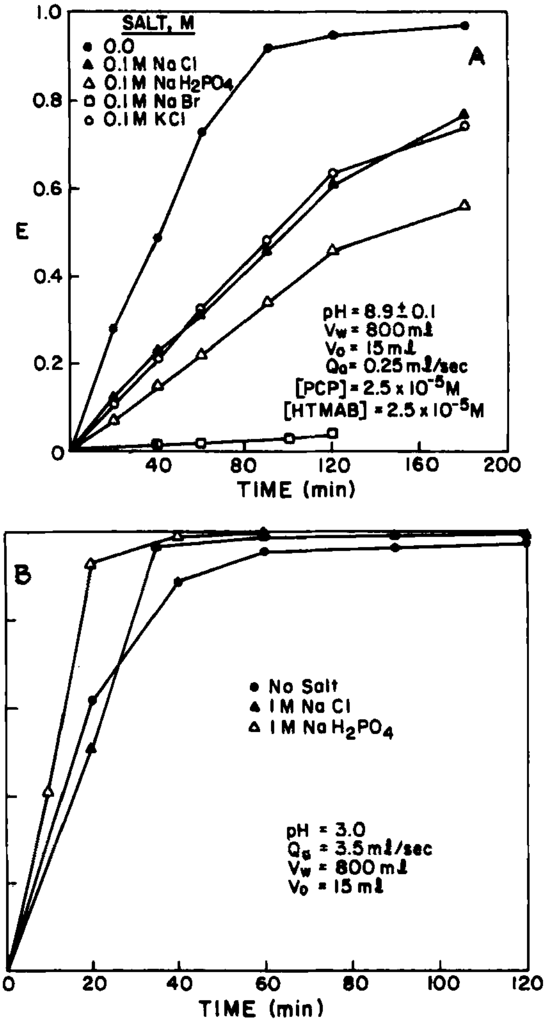

FIG. 17. (A) Effect of various salts on the solvent sublation of PCP + HTMAB complex into decyl alcohol. (B) Effect of various salts on the solvent sublation of neutral PCP into decyl alcohol at pH = 3.0.

prising since similar results on other neutral hydrophobic compounds were described by us earlier (*9*, *10*, *12*, *13*). This is due to a decreasing solubility or increasing hydrophobicity of PCP molecules as a result of the so-called "salting out" effects and can be quantified by using the McDevit-Long theory (*20*). The removal of PCP molecules increases up to 99.9% when 1 *M* NaH_2PO_4 is used in the aqueous phase.

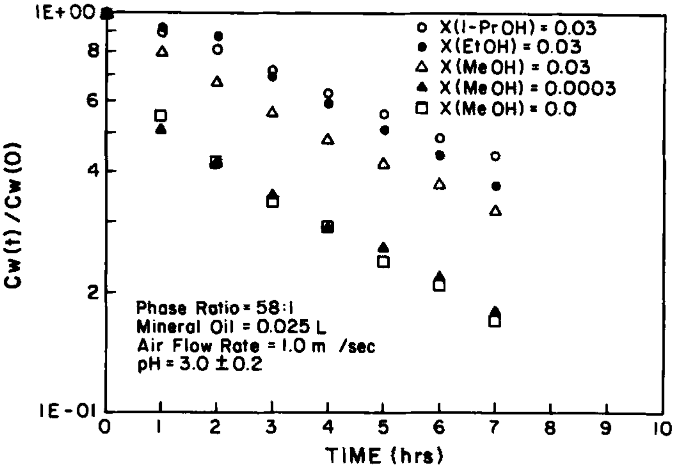

FIG. 18. Effect of various alcohols on the solvent sublation of neutral PCP into mineral oil at pH = 3.0.

The effects of alkyl alcohols on the solvent sublation of neutral PCP molecules from the aqueous phase are shown in Fig. 18. The removal is decreased due to increased solubility or decreased hydrophobicity of PCP molecules in the presence of alcohols in the aqueous phase. This effect increase in the order isopropanol > ethanol > methanol (Fig. 18) in accordance with our theoretical predictions such as those reported earlier for the sublation of trichloroanisole from the aqueous phase (*20*).

The various effects described here, along with comparisons with solvent extraction, effects of solvent volume, air flow rate, and pH, clearly lend support to the overall mechanism proposed for sublation with two competing mechanisms of transport—one exclusively by the bubbles and the other a molecular diffusive transport driven by a concentration difference which tends to return the two phases to an equilibrium condition. Our present effort is directed toward extending the model to a continuous system by conducting experiments to validate the models. These will be reported in subsequent publications.

Acknowledgment

This work was supported by a grant from the National Science Foundation (Grant No. BCS-8822835).

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Received by editor November 21, 1989