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# Removal of Refractory Organics by Aeration. VII. Solvent Sublation of Indene and Aldrin

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**Abstract**

The solvent sublation of indene and aldrin from aqueous systems into mineral oil was studied. With indene, the effects of Ni(II) and Zn(II) were investigated; the usual salting-out effect was observed, with no indication of complex formation between the olefin and the nickelous ion. The effects of a number of alcohols on the solvent sublation of aldrin were determined; very small concentrations of alcohol increase the rate of aldrin removal, while larger concentrations decrease it by roughly an order of magnitude at mole fractions of alcohol of the order of 0.10. Methanol is less effective than ethanol or *n*-propanol in decreasing the removal rate at mole fractions above 0.02.

## INTRODUCTION

Solvent sublation methods, originated by Sebba (*1*), are effective for the removal from aqueous systems of organic compounds which are or can be made hydrophobic. A comprehensive review of this technique was published in 1972 by Karger (*2*); we have published a recent fairly comprehensive review (*3*) and a couple of briefer summaries (*4, 5*). In the area of modeling, Lionel has analyzed the sublation of volatiles (*5*); Womack et al. (*6*) investigated the sublation of neutral molecules, ion pairs, and ion triplets in a single-stage apparatus; and we (*7*) modeled the sublation of surface-active substances in multistage columns. Valsaraj

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developed a method for estimating Langmuir adsorption parameters for hydrophobic organics at air–water interfaces (*8*). The removals of volatile chlorinated organics, PCB's, dichlorobenzenes, nitrophenols, dyes, polynuclear aromatics, alkyl phthalates, and chlorinated pesticides have been studied (*3–10*).

One of the aspects of these separations which has not yet been fully explored is the effects of various solutes on the rate of sublation of the target compound, generally a hydrophobic organic. In some of our previous work we have given cursory attention to this point (*5, 6, 9, 10*). and have observed that an increase in ionic strength typically enhances the rate of removal of a hydrophobic organic, while addition of an organic solvent such as acetone or ethanol to the aqueous phase interferes somewhat with removal. In laboratory separations these effects could be used to enhance removal efficiency and possibly to increase the specificity of a separation. In industrial scale recovery or waste treatment operations, one is mainly concerned about the deleterious effects of organic solvents on removal rates. In either case, additional information about these effects would be helpful.

Here we examine the effect of two divalent cations, nickel(II) and zinc(II), on the rate of removal of the hydrocarbon indene, and the effect of a series of alcohols on the rate of removal of the cyclodiene pesticide aldrin. Indene and the two metals were selected to see if possible complex formation between an olefin and a transition metal via $d$ to $\pi^*$ bonding would interfere with the rate of solvent sublation of the olefin. Aldrin and the alcohols were chosen as representatives of (a) chlorinated organic pesticides, PCB's, etc., and (b) a widely used class of organic solvents which might be expected to be present in wastes considered for treatment by solvent sublation.



## SOLVENT SUBLATION OF INDENE

In most of our earlier work on solvent sublation, the analytical technique employed was gas chromatography, for which the precision was adequate but hardly outstanding. In this study we hoped to use a spectrophotometric technique which would allow us to avoid the extraction step and the inaccuracies of injection. For investigation of possible complexes of olefins and aromatic systems with transition metals, a compound containing these functional groups only was needed; this ruled out most chromophores which absorb strongly in the visible, and suggested chromophores absorbing in the near-ultraviolet. Indene appeared to be an excellent model compound, having both an aromatic

and an olefinic functional group, having slight solubility in water, and having a strongly absorbing chromophore in the near-UV ($\varepsilon$ = 17,300 at $\lambda_{max}$ = 250 nm) (*11*). Indene has been identified as an industrially generated water contaminant (*12*). If one starts a sublation run with a solution having a concentration of about 20 ppm (w/v), one can proceed to 95% removal and still have significant absorbance. At the higher concentrations present in the early stages of the run, however, it is necessary to carry out volumetric dilution in order to achieve acceptable accuracy. The structure of indene is shown in Fig. 1.

There are some weak UV absorbances of inorganic salts in the region of the indene absorption maximum; these are seldom mentioned in the introductory literature because they are rather weak and are generally less enlightening than the absorptions in the visible region characteristic of many transition metal species. While the molar absorptivities of inorganic salts near 250 nm are usually orders of magnitude lower than that of indene, we planned to use orders of magnitude more salt than indene in the solution, so the absorbance of the salts could easily obscure that of indene. Not only salts of transition metals such as Co and Ni, but also salts of alkali and alkaline earth metals exhibit such absorption (*13–15*). A number of absorptivities are given in Volume 5 of the *International Critical Tables* (*16*). One must also note that the anions present may be absorbing, and that the cation absorption is generally affected by the particular anion present (*14*).

The cations selected were Ni(II) and Zn(II); the former is a transition metal ion which might be expected to undergo *d* to $\pi^*$ backbonding with the olefin, while the latter should be less susceptible to complexation. It was anticipated that complexation in the first case might produce a decrease in removal rate, while the salting-out effect observed earlier would enhance removal rate in the second.

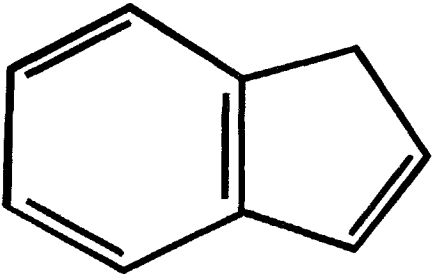

FIG. 1. Indene.

Preliminary tests showed that Ni(II) nitrate exhibited too much absorbance in the spectral region of interest, that Ni(II) chloride was better in this regard, but that Ni(II) sulfate was most satisfactory. The molar absorptivity of Ni(II) sulfate at 250 nm was found to be 0.058 L/mol cm ± 10%. Zinc sulfate was also found to be most suitable, with a molar absorptivity of 0.03 L/mol cm ± 50%. Silver(I), which is known to complex strongly with olefins, has strong absorption bands in the near-UV and was therefore unsuitable for use in this study (*15–17*).

Since we were seeking relative removal rates, it was not necessary to know the absolute concentration of indene, so accurate determination of the molar absorptivity of indene was not necessary. Solutions of indene without added salts were found to obey Beers law over the range from 0.2 to 0.9 in absorptivity. The absorbances of nickel and zinc sulfates were non-Beersian, with absorptivity decreasing with increasing concentration. The absorbances of these salts and indene were not quite additive, but the deviations were easily taken care of by means of a simple empirical fitting of the calibration data. The absorbance of a solution of indene and nickel sulfate tends to be less than the sum of the absorbances of the separate components. Since the concentration of nickel sulfate is over a thousand times that of indene in a typical run, we assigned this to an effect of the nickel ion (and possibly the sulfate) on the indene absorptivity. It was found that the following expression provided an excellent fit to the observed absorbances of indene–nickel sulfate solutions:

$$A_t = (1 - ac_s)\varepsilon_i b c_i + \varepsilon_s b c_s \qquad (1)$$

Here $A_t$ = absorbance; $c_s$ = salt concentration, mol/L; $c_i$ = indene concentration, mol/L; $b$ = path length, cm; $\varepsilon_i$ = 17,300 L/mol cm; $a$ = -0.123 L/mol; and $\varepsilon_s$ = 0.05835 L/mol cm. In our work the interaction correction never exceeded about 7%.

Nonadditivity of absorbances was also observed for mixtures of zinc sulfate and indene, and was handled as described above. The values obtained for $\varepsilon_s$ and $a$ were 0.0195 and 0.0974 L/mol, respectively. The data for this system displayed somewhat more scatter than the data for the nickel sulfate–indene system.

The solvent sublation apparatus used was similar to that described previously (*10*, for example). The addition of a diaphragm gauge between the apparatus and the house air outlet assisted in maintaining constant air flow rates. Air pressures were usually adjusted to about 5 psig, and a

needle valve was then used for fine adjustment. The bubbles were generated by a custom-made sparger having a medium porosity (10 to 15 μm pore size) fritted glass disk 19 mm in diameter and 4 mm thick. The sublation column was 90 cm tall, with an internal diameter of 3.1 cm.

Solutions were prepared as follows. Adrich gold label indene was used, and the metal salts were Fisher reagent grade. Aqueous indene solutions were prepared by dissolving approximately 0.582 g indene in diethyl ether and diluting to 50 mL with diethyl ether in a volumetric flask. This stock solution was stored in a glass vial with a Teflon-lined screw cap which was further sealed (externally) with Parafilm M to further retard evaporation. Diethyl ether is transparent in the UV down to 210 nm (*18*). Aqueous solutions were then prepared by placing 2 mL of the etherial stock solution in a 1000 mL volumetric flask containing approximately 700 mL of distilled water. The flask was stoppered and stirred on a magnetic stirrer for at least 3 h. Then the aqueous solution was made up to volume. Indene solutions were prepared fresh each week. Solutions containing salts and indene were prepared in essentially the same way; the desired quantity of the salt was weighed out, dissolved in distilled water, placed in the volumetric flask, the etherial indene solution added, etc.



The procedure for a sublation run was as follows. The air was turned on, the pressure set with the diaphragm gauge, and the needle valve adjusted to a trial setting. 450 mL of solution was then poured into the column, the air flow rate allowed to stabilize for a minute or so, and then the air flow rate was measured with a soap film flowmeter. The air flow rate was then adjusted to 70 mL/min, and 15 mL of light mineral oil was added at the top of the column. Samples were taken by draining the dead volume of the sampling stopcock (about 3 mL), taking the sample, and recording the time. Air flow was measured after each sample was taken, and, if necessary, the needle valve was adjusted to bring the flow rate back to 70 mL/min.

Samples were collected from a stopcock at the bottom of the column at appropriate intervals (15–30 min) in 6 or 8 dram screw top glass vials which were filled nearly to the top. The caps were lined with aluminum foil and screwed down tightly to avoid evaporative loss. Even with these precautions there was some decrease in absorbance if the samples were stored for more than a day before analysis.

Absorbances at 248.5 nm were obtained on a Cary Model 14 double beam UV-visible spectrophotometer. The spectrum was scanned from 265 to 235 nm. Matched 5 cm quartz cells were used. The last few samples

from each run were dilute enough to be run without further dilution. First-order removal kinetics was assumed, and dilution factors for the more concentrated samples were calculated. Volumetric dilutions with distilled water were then made on these samples; the changes in molar volume upon dilution of these solutions were less than two parts per thousand, which was not significant. Since indene may adsorb on glass, repeated transfers are not advisable (*19*). A single, well-chosen dilution proved suitable for all of the samples studied, and yielded absorbances in the range from 0.3 to 0.9. A representative data set is given in Table 1. All runs were made at a temperature of 25 ± 2°C.

Results for the removal of indene from solutions of indene in water alone, indene in nickel sulfate solution (0.4951 *M*), and indene in zinc sulfate solution (0.5234 *M*) are shown in Fig. 2. The kinetics are first order in all three cases. Slopes to these plots were obtained by linear least squares, and the following values were obtained:

| | |
|---|---|
| $k$ (water alone) | $0.0161 \pm 0.0008$ min$^{-1}$ |
| $k$ (nickel sulfate) | $0.0229 \pm 0.0015$ |
| $k$ (zinc sulfate) | $0.0234 \pm 0.0020$ |



TABLE 1
Solvent Sublation of Indene in the Presence of Nickel Sulfate[a]

| Sample designation | Elapsed time (min) | Composition of diluted sample[b] | Absorbance[c] | Natural log of $\varepsilon_i bc_i$ for original sample[d] |
|---|---|---|---|---|
| A | 0 | 2/20 | 0.564 | 1.808 |
| B | 20 | 3/20 | 0.569 | 1.447 |
| C | 40 | 5/15 | 0.686 | 0.971 |
| D | 60 | 10/10 | 0.790 | 0.392 |
| E | 80 | 10/10 | 0.525 | −0.068 |
| F | 105 | Full strength | 0.686 | −0.550 |
| G | 126 | Full strength | 0.485 | −1.013 |
| H | 150 | Full strength | 0.339 | −1.570 |
| I | 180 | Full strength | 0.278 | −1.947 |
| J | 245 | Full strength | 0.261 | −2.083 |

[a]Concentration of nickel sulfate in undiluted samples is 0.4951 *M*. Samples A through G were used in obtaining the rate constants.

[b]Composition of diluted sample: mL of original sample/mL of added water.

[c]Absorbance of diluted samples.

[d]Natural log of $\varepsilon_i bc_i$ where $\varepsilon_i bc_i$ is calculated using Eq. (1) and scaled back to zero dilution.

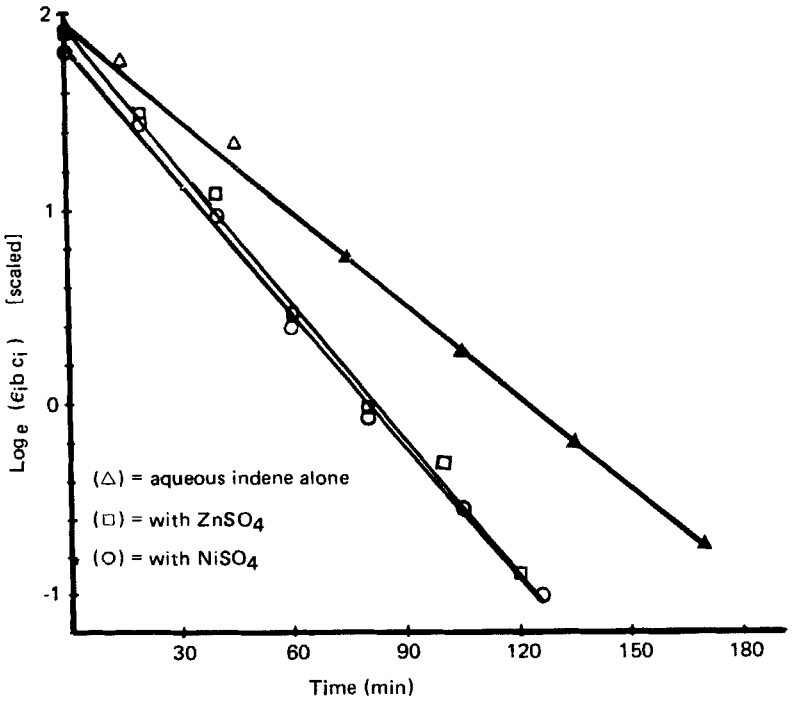


FIG. 2. Solvent sublation of indene alone and in the presence of zinc and nickelous sulfate. The ordinate is the natural log of the corrected absorbance of indene.

## INDENE FINDINGS

The above results are clear, and in some measure are contradictory to our original hypothesis. As expected, the addition of zinc sulfate does significantly enhance the rate of sublation of indene. Contrary to our expectations, however, a solution of nickel sulfate of comparable ionic strength also caused enhancement, statistically indistinguishable from that caused by zinc sulfate. Evidently the effects of any complex formation which may be taking place are much smaller than the effect of the simple salting-out process. Of the other transition metals, the only one which might show a much greater effect than nickel(II) ion is silver(I). Its strong absorption in the near-UV precludes use of our spectrophotometric analysis for indene; removal of Ag(I) by precipitation would still leave the strongly absorbing nitrate ion in solution. This method therefore has not been established as a promising tool for probing weak complexation between olefins and transition metal ions.

Although the above finding is disappointing, it does have a gratifying aspect. It appears that we can expect most transition metal salts to increase the rate of removal of sparingly soluble olefins and aromatics from aqueous solution, which is a desirable finding with regard to the usefulness of the process for the application of solvent sublation to industrial waste treatment.

## ALDRIN

The cyclodiene pesticides aldrin, isodrin, dieldrin, and endrin are thermally and chemically relatively stable, toxic, and relatively long-lived in the environment. They also are lipid-soluble, and tend to concentrate as one moves up a food chain (*20, 21*). They are prepared from hexachlorocyclopentadiene by Diels-Alder reactions. Dieldrin and endrin are produced from aldrin and isodrin by epoxidation of a double bond (*22*). These compounds were banned by EPA in 1974 because of their environmental persistence and carcinogenicity in lab animals (*23*). EPA has given a criterion of 0.71 ng/L as a level of dieldrin which results in an incremental increase of cancer risk of 1/100,000; the corresponding figure for aldrin is 0.74 ng/L. The recommended criterion for endrin is 1.0 μg/L (*24, 25*). Incineration appears to be the method of choice for the destruction of wastes containing these compounds (*23, 26*). Activated carbon treatment is effective for removing these compounds from water, but conventional alum coagulation-sand filtration treatment is not (*27*).



Some of the physical properties of aldrin, dieldrin, and endrin are given in Table 2. These compounds are relatively nonpolar and have quite low solubilities in water; such "hydrophobic" compounds are often readily removed from aqueous systems by solvent sublation. Earlier we developed a method for approximating their adsorption isotherms at air-water interfaces, and found that about 95% of the endrin in a water sample could be removed by solvent sublation treatment for 2 h (*8*). Karger (*2*) has noted that added ethanol affects solvent sublation removal rates; we have also explored the effect of organic solvents on the flotation of naphthalene and phenanthrene (*9*) and phthalate esters (*10*).

Here we present data showing the effects of a series of alcohols on the solvent sublation of aldrin from water into mineral oil. Aldrin was chosen as a prototype cyclodiene pesticide because of the speed with which gas chromatographic analyses for it could be carried out.

A foam flotation column essentially identical to that described in the indene work presented here was used for this study as well. Analyses were

TABLE 2
Physical Properties of Cyclodiene Pesticides

| Pesticide | MW | mp (°C) | Solubility ($H_2O$, 20–25°C, mg/L) | Vapor pressure at 20°C (mmHg) | Henry's law constant[a] at 25°C |
|---|---|---|---|---|---|
| Aldrin | 365 | 104 | 0.01–0.02 | $6.0 \times 10^{-6}$ | 84.9–$1.7 \times 10^3$ |
| Dieldrin | 383 | 175–176 | 0.1–0.25 | $1.78 \times 10^{-7}$ | $2.7 \times 10^4$–$6.8 \times 10^4$ |
| Endrin | 383 | 226–230; decomposes > 200 | 0.23 | $2.7 \times 10^{-7}$ | $3.6 \times 10^4$ |

[a]Henry's law constant: $K_H = \dfrac{\text{aqueous solubility (g/mL)}}{P_{\text{vapor}}\,(\text{mmHg})\,\text{MW}\,5.38 \times 10^{-8}}$



carried out on a Shimadzu GC-Mini-2 gas chromatograph equipped with a Ni-63 electron capture detector. The column was a 30-m glass capillary, coated with SE-30 and run at 200 or 220°C. Injection port-detector temperatures of 220 or 300°C were used. The carrier gas was 99.999% nitrogen.

The alcohols used were methanol, *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, and *t*-butanol (Fisher certified ACS grade), *s*-butanol (Kodak), and ethanol (Aaper 95% USP grade). Aldrin was research-grade pesticide from Supelco and Polyscience. A roughly saturated stock solution of aldrin was prepared by adding 10 mg of aldrin to approximately 4 L of deionized water. This was then stirred magnetically for 1 week, then filtered through a sintered glass funnel and stored in a brown glass bottle in the dark. For each solvent sublation run, 500 mL of aqueous solution was prepared by diluting 100–200 mL of stock solution with deionized water. Methanol, ethanol, or *n*-propanol were added to make the solution 0.01, 0.02, 0.04, 0.05, 0.06, 0.08, or 0.10 mol fraction in the alcohol. Mole fractions of *i*-propanol used were 0.02, 0.05, and 0.10. The butanols are not so soluble in water; mole fractions of the butanols used were 0.005, 0.010, and 0.015. Fisher lab grade paraffin oil was used for the organic solvent layer; paraffin oil is relatively inexpensive, nontoxic, nonvolatile, insoluble in water, and a good solvent for organochlorine pesticides. Fisher pesticide grade hexane was used for the extraction of aldrin from the aqueous samples taken during the course of a run, and Fisher certified ACS grade anhydrous sodium sulfate was used for drying the hexane extracts.

Runs were made as follows. At the beginning of each run the air was turned on, the column drain stopcock was closed, and the solution to be treated was shaken thoroughly. The column was first filled with deionized water or a water/ethanol mixture (in case alcohols were to be present in the solution to be treated) and the air flow rate was adjusted with a needle valve and soap film flowmeter. The column was then drained, rinsed, and filled with approximately 575 mL of the solution to be treated. A 10–15 mL portion of mineral oil was poured on top of the aqueous phase in the column, and the air flow rate checked and, if necessary, adjusted to 100 mL/min. Ten mL samples of the aqueous phase were taken at the beginning of the run and at 15-min intervals for the first 2 h of the run, then at 30-min intervals for the last 2 h. The stopcock was purged before taking each sample. Samples were placed in 4-dram glass vials and sealed with aluminum foil under the plastic screw cap. The air flow rate was checked and adjusted after each sampling. After each run the column was scrubbed with Alconox, rinsed with an ethanol–water solution, and then rinsed with deionized water. One run was made without a mineral oil supernatant layer or added alcohol (aeration), during which the column was vented into a hood. And a sublation run was made with no added alcohols for comparison with the other runs. All runs were made at 25–27°C.



The 10-mL samples were prepared for gas chromatographic analysis by extraction with 1 mL of pesticide-grade hexane (manual shaking for 1 min). Whenever necessary, a small amount of anhydrous sodium sulfate was added to improve separation of the aqueous and hexane layers. The hexane layer was then transferred by pipet to another 4-dram vial to which a small amount of anhydrous sodium sulfate had been added to ensure dryness of the hexane extract. Samples of lowest aldrin concentration were processed first to reduce the chance of contamination of the more dilute samples.

Aldrin standards were prepared in hexane (500, 200, 100, 50, 20, and 10 μg/L, ppb) to check instrument response. Glass stoppers were used in the volumetric flasks containing the standards to avoid contamination or absorption of aldrin from plastic stoppers. Samples and standards were injected by means of the solvent push technique; a 10-μL syringe was first loaded with 2 μL hexane, followed by 1.0 μL sample, and the whole charge then injected into the chromatograph. Each sample was injected two or more times.

The line peaks produced on the strip-chart recorder were measured with a metric ruler and averaged for each sample. The peak height of the sample taken at the beginning of each run was divided by the peak heights of all the other samples taken during the run, and the natural logs

of the quotients calculated and plotted versus time to give the removal curves. Linear least squares fits for the first hour of each run were obtained; the slopes of these lines give the first-order rate constants for the removal of aldrin.

## ALDRIN RESULTS

All of the aeration and solvent sublation runs were made on the same apparatus under essentially the same conditions of volume, air flow rate, and temperature. The bubbles generated during the aeration and sublation runs without added alcohol were, however, considerably larger and fewer than those generated during the runs in which the column charge contained alcohol. One run was made with a very small amount of added ethanol (0.0003 mol fraction) to demonstrate the effect of small bubble size on solvent sublation; the removal rate was substantially enhanced over that for a column charge containing no alcohol.

During the runs with propanols and butanols, 0.5–1.5 cm of froth was observed above the supernatant mineral oil layer in the column. Larger mole fractions of the propanols and butanols caused the mineral oil layer to break up into globules, the size of which decreased with increasing mole fraction of alcohol. During runs with 0.08 and 0.10 *n*-propanol, 0.10 *i*-propanol, and 0.015 *i*-butanol, mineral oil globules were observed moving around in the upper portion of the aqueous phase in the sublation column. However, there was no evidence of a mineral oil peak on the corresponding gas chromatograms, so backmixing must not have been very extensive.

Because of the fluctuations in the house air pressure, it was difficult to keep the air flow constant; this problem led to the inclusion of a diaphragm pressure valve in the apparatus before the indene work was done. The flow rate reported on a representative run is therefore an average for the run.

All samples were analyzed on the same gas chromatograph and capillary column. Generally the column temperature was 220°C; for runs with propanols or butanols, a temperature of 200°C was used to prevent overlapping of the alcohol peak tail with the aldrin peak.

Since it was necessary to dry the extracted samples before analysis, it was feared that transfer of the hexane phase and treatment with sodium sulfate would cause loss of aldrin, which tends to adsorb strongly from aqueous solution. Analysis of samples before and after transfer and drying showed no significant difference; evidently adsorption from hexane solutions is not a serious problem. Samples which were kept for

several days before analysis sometimes showed erratic results, apparently due to evaporation past an inadequately sealed vial closure.

We next show a few representative plots of runs. Figure 3 shows the removal of aldrin by simple aeration, with no mineral oil supernate nor any alcohol in the aqueous phase. Figure 4 shows the solvent sublation curve for aldrin removal in the absence of alcohols. Figure 5 shows a run made with 0.02 mol fraction of methanol. In Fig. 6 we see a run made with 0.10 mol fraction of methanol, in which we can qualitatively see substantial reduction in solvent sublation efficiency. We observe a rather

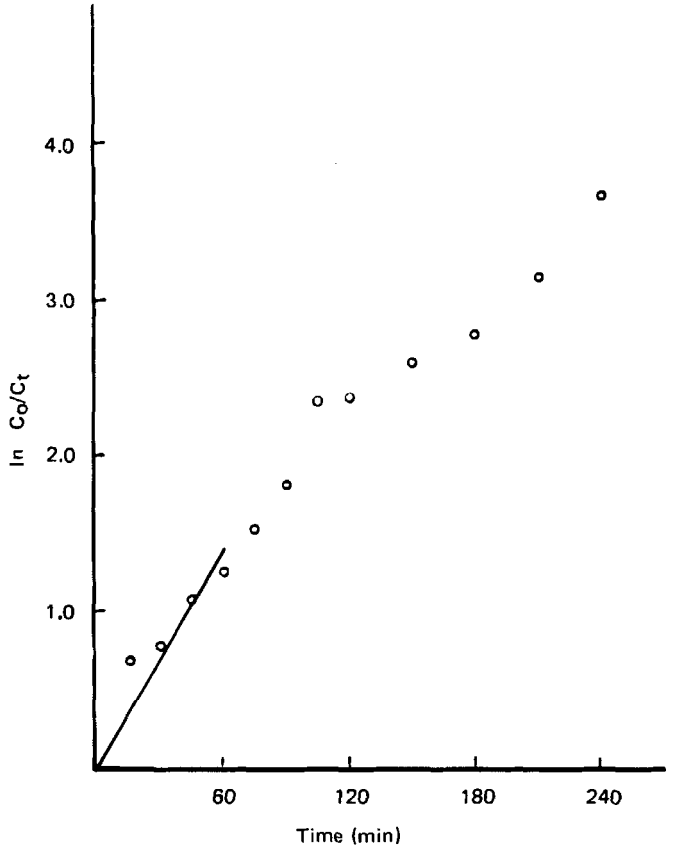


FIG. 3. Removal curve for simple aeration of aldrin. No added alcohols. Average air flow rate, 100.6 mL/min.

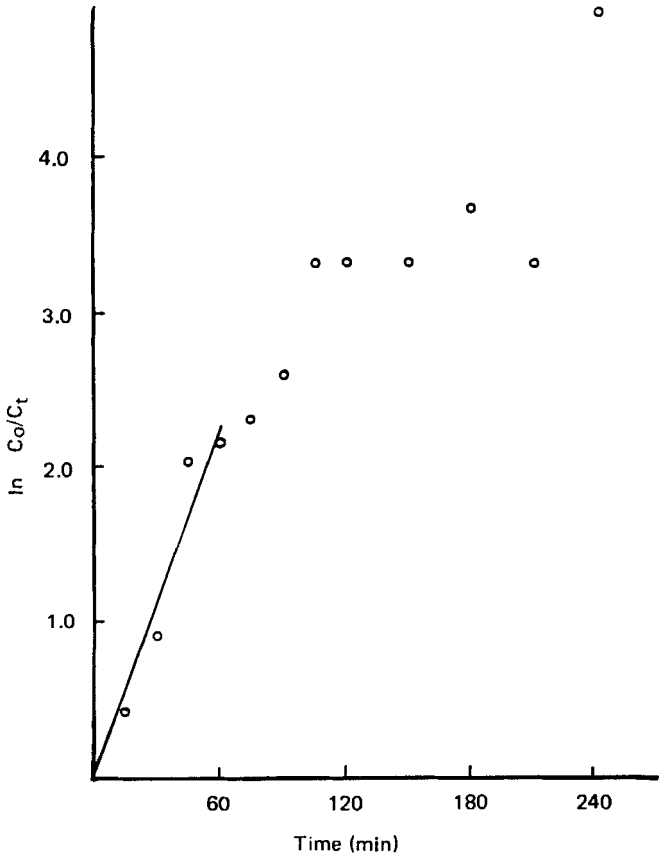


FIG. 4. Removal curve for solvent sublation of aldrin with no added alcohols. Air flow rate, 97.3 mL/min.

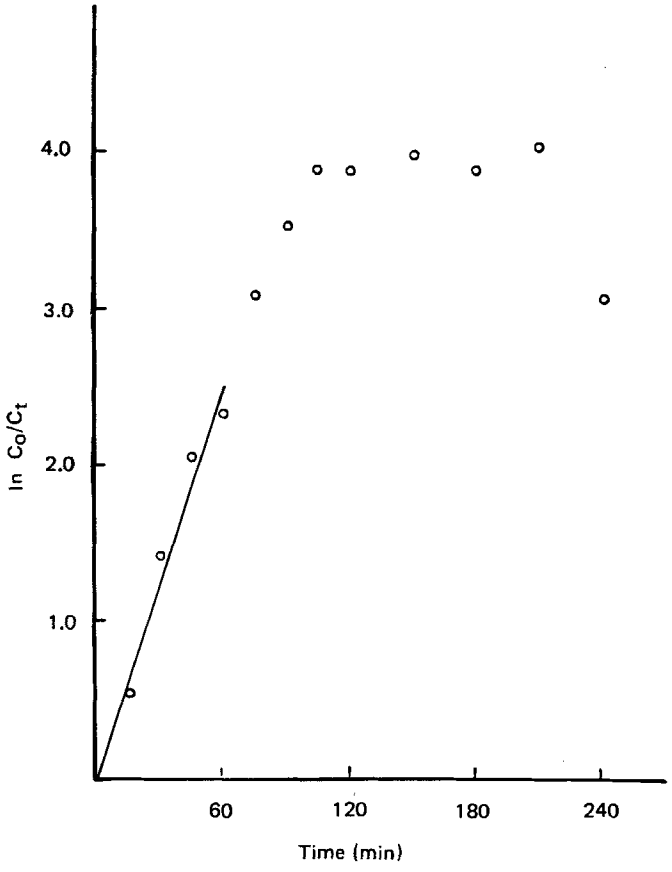


FIG 5. Removal curve for solvent sublation of aldrin. The aqueous solution contains 0.02 mol fraction methanol. Air flow rate, 101.1 mL/min.

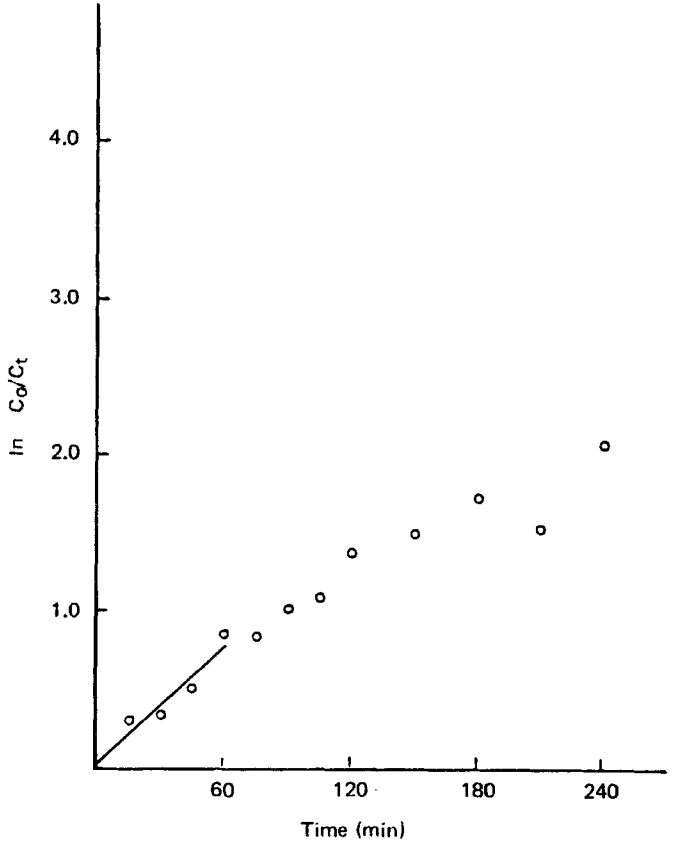


FIG 6. Removal curve for solvent sublation of aldrin. Aqueous solution contains 0.10 mol fraction methanol. Air flow rate, 100.0 mL/min.

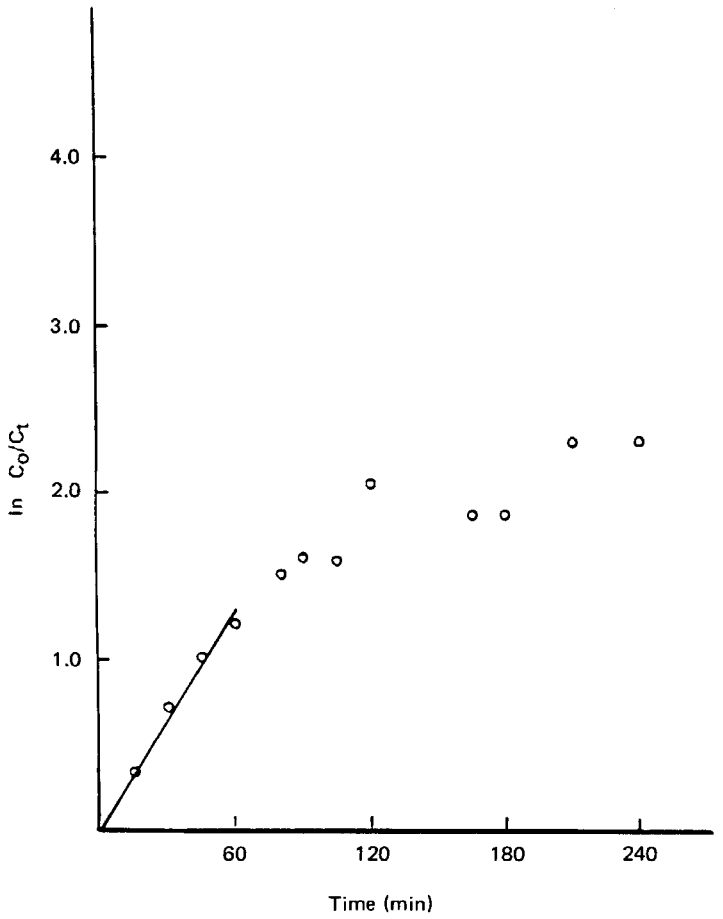


FIG 7. Removal curve for solvent sublation of aldrin. Aqueous solution contains 0.015 mol fraction of *n*-butanol. Air flow rate, 98.9 mL/min.

substantial reduction in efficiency with only 0.015 mol fraction of *n*-butanol in Fig. 7. These runs give some idea of the range over which the kinetics can be reasonably approximated as first order, and the dispersion in the data. A total of 39 runs was made.

The results of this work are summarized in Tables 3 and 4. In Table 3 we give the percent aldrin removed after 1 and 2 h of sublation for the various solutions. In Table 4 the first-order rate constants and their standard deviations for these runs are given.

These results exhibit a number of interesting features. First, the rate of removal by sublation is some 60% larger than the rate of removal by simple aeration, indicating that a quite substantial fraction of the aldrin is removed on the surfaces of the bubbles. Second, the rate of removal of aldrin is actually enhanced by the presence of small quantities of alcohols. This may be due to several causes. We observed that the addition of even quite small amounts of alcohols resulted in a very marked decrease in the sizes of the bubbles; this increases the amount of air–water interface passing through the column and also increases the contact time of the individual bubbles, both of which should increase the removal rate. The decrease in bubble size is due to a decrease in the surface tension of the water when alcohols are added (*28, 29*). Another cause is the ability of small concentrations of alcohols to enhance the hydrogen bonding structure of water. Ben-Naim (*30*) showed that mole fractions of ethanol below 0.03 increase the hydrogen bonding of water, which should tend to decrease the solubility of a hydrophobic solute such as aldrin. This, in turn, should increase the tendency of the aldrin molecules to concentrate at air–solution interfaces, thereby increasing the rate of removal by solvent sublation.

At higher alcohol concentrations, the hydrogen-bonded water structure is progressively more broken down and the solution phase becomes less polar; both of these effects should increase the solubility of aldrin which, as we have noted earlier, is several orders of magnitude more soluble in aliphatic alcohols than it is in pure water. (See Table 5.) One might also expect the formation of hemimicelles of alcohol molecules around an aldrin molecule, hydrocarbon tails van der Waals bonding to the aldrin, and OH groups hydrogen bonding to the water; such structures should enhance the solubility of aldrin in alcohol–water mixtures. Any effect increasing the solubility of aldrin should tend to reduce the extent of its being "squeezed out" of the solvent structure and segregated on air–water (and possibly container–water) interfaces, thereby decreasing the rate of removal by solvent sublation. Our results indicate that, other things being equal, the longer the chain length of the alcohol, the more effective it is in

TABLE 3
Percentage of Aldrin Removed by Solvent Sublation with and without Added Alcohols

| Alcohol mole fraction | % Removed after 1 h | % Removed after 2 h |
|---|---|---|
| Aeration: | | |
| 0.00 | 71.7 | 90.7 |
| Sublation: | | |
| 0.00 | 88.3 | 96.5 |
| Methanol: | | |
| 0.01 | 90.1 | 97.5 |
| 0.02 | 90.2 | 98.0 |
| 0.04 | 86.1 | 94.8 |
| 0.05 | 77.1 | 89.4 |
| 0.06 | 93.8 | 97.1 |
| 0.08 | 39.7 | 73.3 |
| 0.10 | 56.6 | 74.9 |
| Ethanol: | | |
| 0.0003 | 96.6 | 99.0 |
| 0.01 | 94.8 | 96.3 |
| 0.02 | 94.9 | 97.7 |
| 0.04 | 75.6 | 88.0 |
| 0.05 | 69.9 | 88.5 |
| 0.06 | 63.4 | 81.9 |
| 0.08 | 45.6 | 62.6 |
| 0.10 | 8.8 | 34.6 |
| *n*-Propanol: | | |
| 0.01 | 75.7 | 91.9 |
| 0.02 | 43.2 | 64.1 |
| 0.04 | 55.9 | 71.2 |
| 0.05 | 20.0 | 48.2 |
| 0.06 | 24.8 | 48.0 |
| 0.08 | 28.8 | 53.7 |
| 0.10 | 33.8 | 56.5 |
| *i*-Propanol: | | |
| 0.02 | 66.7 | 85.3 |
| 0.05 | 30.4 | 54.2 |
| 0.10 | 22.6 | 40.5 |
| *n*-Butanol: | | |
| 0.005 | 83.3 | 95.7 |
| 0.010 | 70.9 | 87.5 |
| 0.015 | 88.9 | 96.7 |
| *s*-Butanol: | | |
| 0.005 | 79.5 | 89.5 |
| 0.010 | 62.2 | 83.5 |
| 0.015 | 55.3 | 73.1 |
| *i*-Butanol: | | |
| 0.005 | 94.9 | 98.1 |
| 0.010 | 93.3 | 97.1 |
| 0.015 | 85.9 | 87.8 |
| *t*-Butanol: | | |
| 0.005 | 91.7 | 96.7 |
| 0.010 | 76.2 | 90.6 |
| 0.015 | 69.4 | 85.2 |

TABLE 4
Calculated First-Order Rate Constants with Statistical Information for the Removal of Aldrin from Aqueous Solution by Solvent Sublation

| Alcohol mole fraction | Rate constant,[a] $k \times 10^{-2}$ ($min^{1}$) | Standard deviation, ( ) $\times 10^{-3}$ | Variance $\times 10^{-2}$ | 95% Confidence limits, ( ) $\times 10^{-4}$ |
|---|---|---|---|---|
| Aeration: | | | | |
| 0.00 | 2.34 | 2.55 | 4.39 | 5.94 |
| Sublation | | | | |
| 0.00 | 3.76 | 3.18 | 6.82 | 7.39 |
| Methanol: | | | | |
| 0.01 | 4.47* | 4.17 | 11.7 | 9.68 |
| 0.02 | 4.18* | 2.19 | 3.24 | 5.09 |
| 0.04 | 3.28 | 0.568 | 0.217 | — |
| 0.05 | 2.49 | 2.23 | 3.36 | — |
| 0.06 | 4.71* | 9.59 | 62.0 | 22.3 |
| 0.08 | 1.12 | 1.71 | 1.97 | — |
| 0.10 | 1.26 | 1.07 | 0.775 | — |
| Ethanol: | | | | |
| 0.0003 | 6.73* | 8.91 | 53.6 | 20.7 |
| 0.01 | 5.39* | 4.41 | 11.4 | 13.8 |
| 0.02 | 5.66* | 5.05 | 17.2 | 17.0 |
| 0.04 | 2.55 | 1.95 | 2.22 | — |
| 0.05 | 2.34 | 1.62 | 1.78 | — |
| 0.06 | 1.92 | 2.28 | 3.49 | — |
| 0.08 | 1.01 | 0.589 | 0.203 | — |
| 0.10 | 0.259 | 0.704 | 0.335 | — |
| *n*-Propanol: | | | | |
| 0.01 | 2.55 | 1.30 | 1.14 | 3.02 |
| 0.02 | 0.941 | 0.357 | 0.861 | 0.830 |
| 0.04 | 1.41 | 1.27 | 1.09 | — |
| 0.05 | 0.389 | 0.320 | 0.069 | — |
| 0.06 | 0.441 | 0.604 | 0.246 | — |
| 0.08 | 0.537 | 0.471 | 0.150 | — |
| 0.10 | 0.600 | 0.555 | 0.208 | — |
| *i*-Propanol: | | | | |
| 0.02 | 2.11 | 1.77 | 2.11 | 4.11 |
| 0.05 | 0.518 | 0.750 | 0.380 | — |
| 0.10 | 0.398 | 0.693 | 0.324 | — |
| *n*-Butanol: | | | | |
| 0.005 | 3.77 | 5.73 | 22.1 | 13.3 |
| 0.010 | 2.18 | 0.800 | 0.432 | 1.86 |
| 0.015 | 3.84 | 1.09 | 0.797 | 2.53 |
| *s*-Butanol: | | | | |
| 0.005 | 2.74 | 1.84 | 2.29 | — |
| 0.010 | 1.68 | 0.949 | 0.608 | 2.21 |
| 0.015 | 1.36 | 0.852 | 0.490 | — |

(*continued*)

TABLE 4 (continued)

| Alcohol mole fraction | Rate constant,[a] $k \times 10^{-2}$ ($min^1$) | Standard deviation, ( ) $\times 10^{-3}$ | Variance $\times 10^{-2}$ | 95% Confidence limits, ( ) $\times 10^{-4}$ |
|---|---|---|---|---|
| *i*-Butanol: | | | | |
| 0.005 | 5.55* | 5.41 | 19.7 | 12.6 |
| 0.010 | 5.60* | 15.8 | 117 | 44.2 |
| 0.015 | 4.12* | 8.62 | 50.1 | 20.0 |
| *t*-Butanol: | | | | |
| 0.005 | 4.55* | 3.90 | 10.2 | 9.04 |
| 0.010 | 2.72 | 2.11 | 3.01 | 4.91 |
| 0.015 | 2.25 | 2.77 | 5.16 | — |

[a]Asterisks indicate rate constants greater than that for solvent sublation with no added alcohol.



reducing the removal rate. Thus methanol is less effective than ethanol which is less effective than *n*-propanol at interfering with the separation at mole fractions greater than 0.02. The results obtained using butanols exhibited a good deal of scatter, but there does seem to be some enhancement of removal rates at low alcohol concentrations. Ethanol and the propanols at mole fractions of around 0.10 reduce sublation rates by roughly an order of magnitude; the effect of methanol was significantly less.

We conclude that the presence of substantial quantities of organic solvents may seriously interfere with the removal of hydrophobic organics by solvent sublation, and that this point should be explored if solvent sublation is being considered for use in the removal of hydrophobic organics from aqueous systems.

TABLE 5
Solubility of Aldrin in Aliphatic Alcohols

| | g Aldrin/100 mL alcohol at 25°C |
|---|---|
| Methanol | 5 |
| Ethanol | 5 |
| *i*-Propanol | 4 |
| *n*-Butanol | 9 |

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