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Removal of Refractory Organics by Aeration. VI. Solvent Sublation of Alkyl Phthalates

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Abstract

The solvent sublation of diethyl, di-*n*-butyl, and bis(2-ethylhexyl) phthalates in a batch-type laboratory scale apparatus is reported. Removals of all three are accelerated by added NaCl and markedly decreased by ethanol. The rate of removal of diethyl phthalate is much slower than the rates of removal of di-*n*-butyl and bis(2-ethylhexyl) phthalates.

INTRODUCTION

Solvent sublation techniques, first used by Sebba (*1*), have some promise for the removal of certain types of organic compounds from aqueous systems. Karger published a comprehensive review of the subject in 1972 (*2*); we have briefly reviewed the more recent literature (*3, 4*) and published a recent fairly comprehensive review (*5*). Lionel et al. (*3*) modeled the sublation of volatiles; Womack et al. (*4*) analyzed the solvent sublation of neutral molecules, ion pairs, and ion triplets in a single-stage apparatus. We (*6*) modeled the sublation of surface-active substances in multistage columns, and developed a method for estimating Langmuir adsorption parameters for hydrophobic organics at air–water interfaces (*7*). Removals of volatile chlorinated organics, PBC's dichlorobenzenes, nitrophenols, dyes, polynuclear aromatics, and chlorinated pesticides have been studied (*3–8*).

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Phthalate esters are produced in substantial quantities in the United States (some 1.2×10^9 lb in 1977), with bis(2-ethylhexyl) phthalate and diisodecyl phthalate being produced in the largest amounts (3.9×10^8 and 1.6×10^8 lb, respectively). The principal use of these compounds is as plasticizers, with building and construction, home furnishings, and the automotive industry being the three largest users. Nonplasticizer applications account for a little over 5% of their total use (*9*).

The phthalate esters are among the less toxic industrial organic contaminants found in water. The ambient water criteria for protection of human health from the toxic properties of these compounds ingested through water and contaminated aquatic organisms are as follows: diethyl phthalate, 350 mg/L; dibutyl phthalate, 34 mg/L; bis(2-ethylhexyl) phthalate, 15 mg/L. The toxicities of these compounds are reviewed in EPA's water quality criteria document for the phthalate esters (*8*).

The solubilities of these three esters in water are quite low; all are listed as "insoluble" in the phthalate ester water quality criteria document (*8*). This makes them likely candidates for removal from aqueous systems by solvent sublation. We discuss here the solvent sublation of these three phthalate esters into mineral oil in a batch lab-scale apparatus. The effects of added NaCl and of added ethanol, of air flow rate, and of mass transfer from the mineral oil back into the aqueous phase are investigated.

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EXPERIMENTAL

A batch-type laboratory scale solvent sublation column was used for all runs; this apparatus is diagrammed in Fig. 1. The Pyrex glass column is 90 cm long by 3.6 cm in diameter, and is closed at the bottom by a stopper mounting the air dispersion head (a 1.2-cm diameter "fine" porosity frit) and a stopcock for removing samples. House air was passed through a water saturator and glass wool filter before going to the air dispersion head. Airflow rates were controlled with a Nupro micrometer needle valve and were measured with a soap film flowmeter and stopwatch. All runs were made at room temperature (22°C).

The chemicals used were as follows. Diethyl phthalate, J. T. Baker Practical grade; dibutyl phthalate, Fisher Scientific Reagent grade; bis(2-ethylhexyl) phthalate, Eastman Practical grade; 95% ethanol, Aaper Alcohol and Chemical Co. Reagent quality; sodium chloride, Fisher Certified A.C.S. grade; and paraffin oil, Fisher Scientific Laboratory grade.

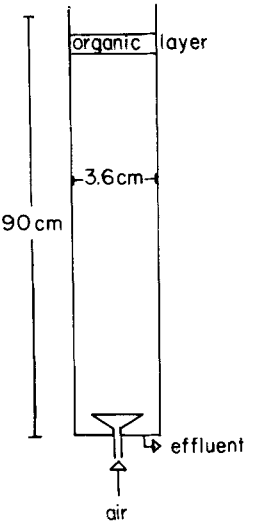

FIG. 1. The apparatus.

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Saturated stock solutions of the phthalates were made up in deionized water. Standard solutions of the phthalates were prepared in pesticide grade hexane; see Table 1. Analyses were carried out on a Shimadzu GC Mini-2 gas chromatograph with a flame ionization detector; a 30-m capillary column coated with SE30 and operated at the temperatures indicated in Table 1 was used. Peak areas were measured with a Shimadzu R1B electronic integrator.

Runs were made as follows. A 600-mL portion of test solution was prepared by diluting an appropriate volume of phthalate stock solution with deionized water, adding the desired quantity of NaCl or ethanol, and diluting to volume. The test solution was then poured into the column, 10 mL of paraffin oil was added, and the timer was started. Samples were taken at regular intervals (as seen on the figures, these ranged from 2 to as much as 30 min), and the airflow rate was measured after each sample was taken. The samples were extracted with pesticide grade hexane, and μL portions were then injected into the gas chromatograph by the solvent push technique. The instrument was frequently calibrated by injecting standards. See Table 1.

The runs listed in Table 2 were made for each of the alkyl phthalates.

TABLE 1
Gas Chromatograph Analysis Conditions

Compound	Column temperature (°C)	Aqueous sample (mL)	Hexane volume (mL)	Injection volume (μL)
Diethyl phthalate	105	10	2	1
Dibutyl phthalate	150	50	1	3
Bis(2-ethylhexyl) phthalate	235	100	1	8

Phthalate Standards in Hexane (g/L)

Diethyl phthalate: 4.0, 2.0, 1.0, 0.5, 0.1
Dibutyl phthalate: 1.0, 0.5, 0.1
Bis(2-ethylhexyl) phthalate: 1.0, 0.5, 0.1, 0.05

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RESULTS

The results of these runs are shown graphically in Figs. 2–11 as plots of $\log_e$ [initial concentration/concentration at time t] in order to highlight departures from first-order removal rates.

Data for diethyl phthalate are presented in Figs. 2–5. In Fig. 2 we see that the time required to remove half of the solute under the conditions of these experiments is of the order of 2 h. Decreasing the airflow rate from 90

TABLE 2
Operating Conditions of Runs

Approximate air flow rate (mL/min)	Solution
100	No NaCl, no EtOH
100	4.76% NaCl
100	2.44% NaCl
100	0.01 mol fraction EtOH
100	0.02 mol fraction EtOH
100	0.04 mol fraction EtOH
100	0.06 mol fraction EtOH
100	0.08 mol fraction EtOH
100	0.10 mol fraction EtOH
50	No NaCl, no EtOH

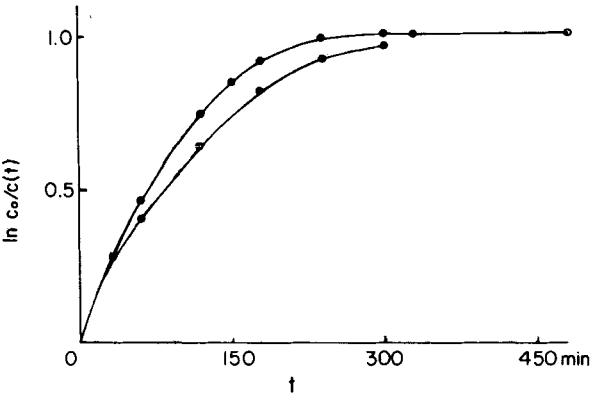

FIG. 2. Solvent sublation of diethyl phthalate. Effect of airflow rate. (Upper curve) 90.0 mL/min; (lower curve) 48.3 mL/min.

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to 48 mL/min did not result in a corresponding decrease in removal rate; we believe that this is due to the decreased size of the bubbles at the lower flow rate. Smaller bubbles are more efficient at solvent sublation than are larger bubbles; they rise more slowly, so have a longer contact time with the solution, and they have a larger surface-to-volume ratio than larger bubbles.

The upper curve in Fig. 2 and the curves in Fig. 3 exhibit the effect of added NaCl on the rate of removal of diethyl phthalate by solvent

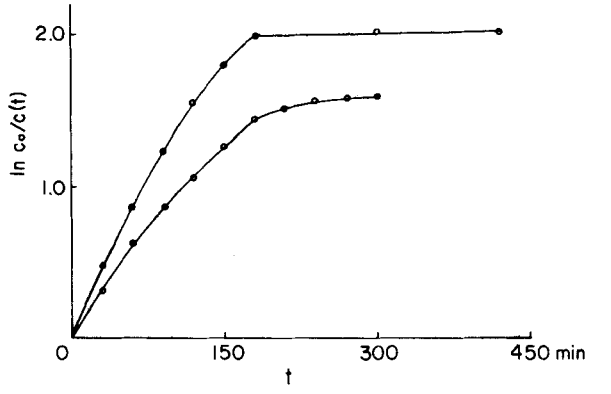

FIG. 3. Solvent sublation of diethyl phthalate. Effect of added NaCl. (Upper curve) 97.7 mL air/min, 4.76% NaCl; (lower curve) 107 mL air/min, 2.44% NaCl.

sublation. The time required to remove half of the solute is reduced from about 108 min (no salt) to about 45 min (4.76% salt). This effect, which we have observed with other organic solutes and other salts (*7*), is presumably caused by the same decrease in solubility utilized by organic chemists in "salting out" an organic product from an aqueous phase.

The upper curve in Fig. 2 and the plots shown in Fig. 4 show the impact of added ethanol on the rate of solvent sublation of diethyl phthalate. Even relatively small amounts of ethanol drastically reduce the removal rate of this compound. We note that the effect here is substantially greater than we had previously observed with naphthalene (*8*).

The departure of these semilog plots from linearity (all are concave downward) suggested that we were getting some mass transfer of diethyl phthalate from the mineral oil layer back into the water layer. The pair of runs plotted in Fig. 5 shows that this is indeed the case. In run 11 the oil layer was removed by pipette after 180 min of sublation and replaced with a fresh portion of paraffin oil. This resulted in a very substantial increase in the removal rate, as one would have expected if reverse mass transfer were responsible for the leveling out of these curves.

Figures 6 through 8 show the results of solvent sublation runs with dibutyl phthalate. Removal rates are far more rapid than were those for diethyl phthalate; the time required for 50% removal of dibutyl phthalate with an airflow rate of about 99 mL/min is about 4.1 min; with a flow rate of 48 mL/min, it is about 7 min. Backdiffusion is also less of a problem, and about 98% of the solute is removed in 20 min with an airflow rate of 99 mL/min, as seen in Fig. 6. The curves exhibit first-order kinetics to a quite reasonable approximation.

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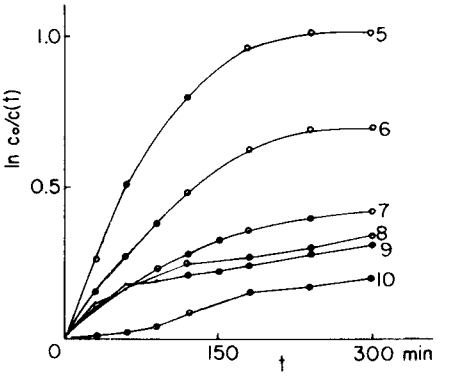

FIG. 4. Solvent sublation of diethyl phthalate. Effect of added ethanol. (5 to 10) 0.01, 0.02, 0.04, 0.06, 0.08 and 0.10 mol fraction ethanol.

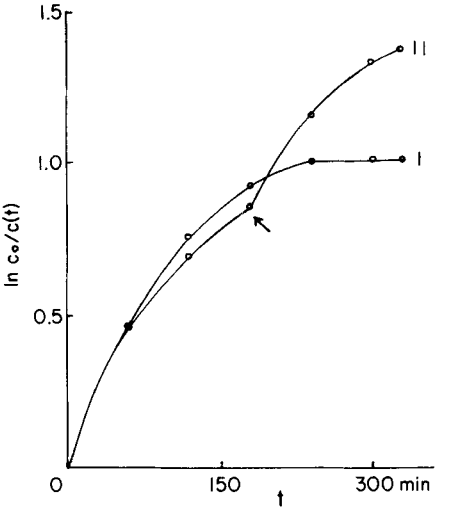

FIG. 5. Solvent sublation of diethyl phthalate. Effect of replacing the oil layer after 180 min. (I) 90.0 mL air/min; (II) 100 mL air/min, oil exchanged at 180 min.

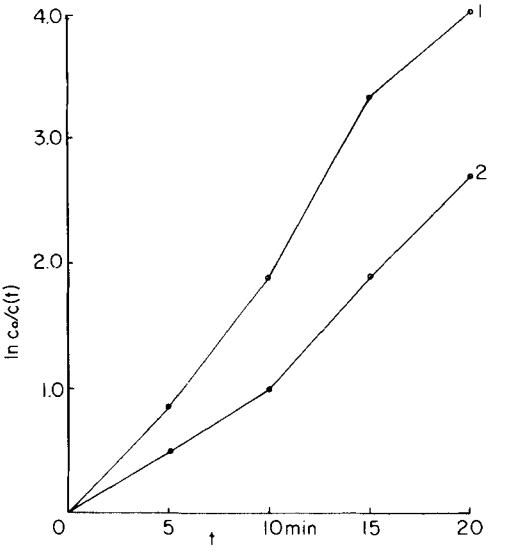

FIG. 6. Solvent sublation of di-*n*-dubyl phthalate. Effect of airflow rate. (1) 98.7 mL air/min; (2) 47.7 mL air/min.

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The effect of added sodium chloride is seen by comparing curve 1, Fig. 6 (no salt) with the two curves shown in Fig. 7 (2.44 and 4.76% NaCl). The time required for 50% removal decreases from 4.0 to 2.4 min as the NaCl concentration is increased from 0 to 4.76%.

Ethanol decreases the rate of solvent sublation of dibutyl phthalate quite spectacularly, as seen by comparing curve 1, Fig. 6 (no ethanol) with the curves displayed in Fig. 8 (mole fractions of EtOH of 0.01, 0.02, 0.04, 0.06, 0.08, and 0.10). The mole fractions ethanol and the corresponding times required to remove 50% of the dibutyl phthalate are 0, 4 min; 0.01, 3.8 min; 0.02, 9 min. For mole fractions of 0.04 and above, less than half of the dibutyl phthalate was removed after 20 min of treatment.

The effect of airflow rate on the solvent sublation of bis(2-ethylhexyl) phthalate is shown in Fig. 9. Half-lives for removal of this compound from water were very short—about a minute at an airflow rate of 101 mL/min, roughly 1.2 min at 49 mL/min. Slight enhancement of removal rates is found with added NaCl, as seen in Fig. 10. The presence of ethanol at mole fractions in the range 0.01 to 0.10 is seen to reduce the rate of solvent sublation of bis(2-ethylhexyl) phthalate substantially, as shown in Fig. 11;

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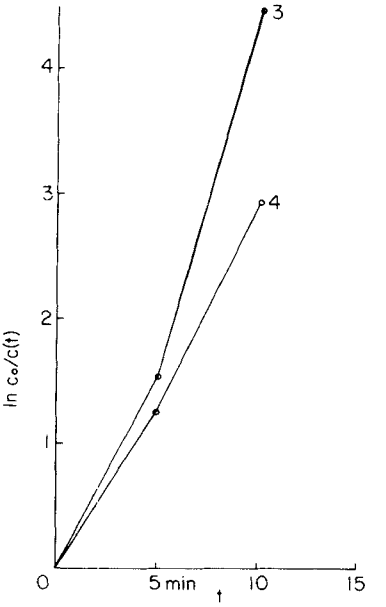

FIG. 7. Solvent sublation of di-*n*-butyl phthalate. Effect of added NaCl. 100 mL air/min; (3) 4.76% NaCl; (4) 2.44% NaCl.

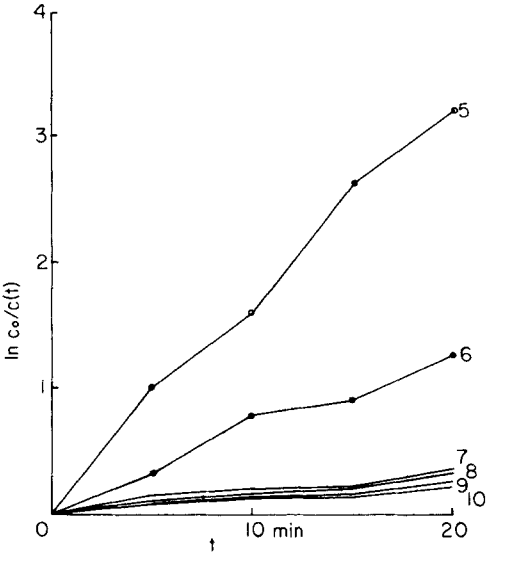

FIG. 8. Solvent sublation of di-*n*-butyl phthalate. Effect of added ethanol. 100 mL/min airflow; (5 to 10); mole fraction ethanol = 0.01, 0.02, 0.04, 0.06, 0.08, and 0.10.

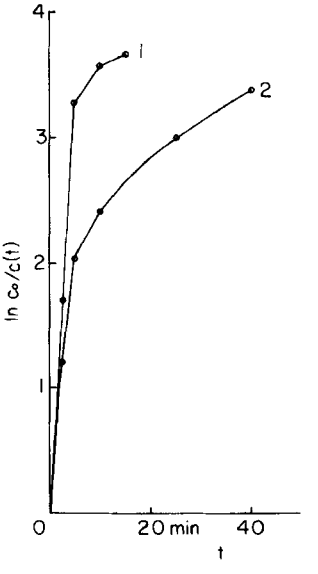

FIG. 9. Solvent sublation of bis(2-ethylhexyl) phthalate. Effect of airflow rate. (1) 101.4 mL/min; (2) 48.9 mL/min.

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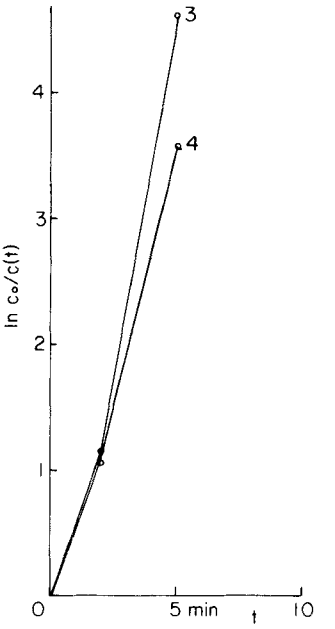

FIG. 10. Solvent sublation of bis(2-ethylhexyl) phthalate. Effect of added NaCl. Airflow = 102 mL/min; (3) 4.76% NaCl; (4) 2.44% Nacl.

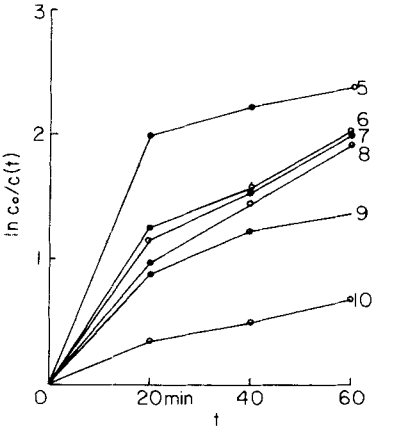

FIG. 11. Solvent sublation of bis(2-ethylhexyl) phthalate. Effect of added ethanol. Airflow = 102 mL/min; (5 to 10); mole fraction ethanol = 0.01, 0.02, 0.04, 0.06, 0.08, and 0.10.

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even the presence of 0.01 mol fraction increases the half-life for removal from about 1 min to about 6 min.

We draw the following conclusions on the basis of the above results.

(1) Diethyl phthalate (and presumably dimethyl phthalate as well) is too soluble in water to be rapidly removed by solvent sublation. Backmixing from the organic layer is also a problem with diethyl phthalate.
(2) Di-*n*-butyl phthalate and bis(2-ethylhexyl) phthalate (and presumably the other alkyl phthalates with alkyl groups at least as large as *n*-butyl) are rapidly removed from water by solvent sublation.
(3) The presence of sodium chloride (and presumably other salts as well) enhances solvent sublation removal rates somewhat.
(4) The presence of ethanol at concentrations of less than 0.1 mol fraction drastically reduces the rate of solvent sublation of alkyl phthalates, to the point of making it useless as a practical separation from media containing ethanol.

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