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Purification of Tetracene: Vapor Zone Refining and Eutectic Zone Melting

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Abstract—Impurities present in tetracene have been concentrated by vapor zone refining, and identified by chromatography and absorption and mass spectroscopy. They include anthracene, pyrene, methylpyrene, chrysene, 5,12-dihydrotetracene, 1,2-benzodiphenylene oxide, 1,2-benzodiphenylene sulfide, brasan, 2,3-benzofluorene, 4,5-iminophenanthrene and 5,12-tetracenequinone.

Eutectic mixtures of tetracene with 2-naphthoic acid have been zone melted, and numerous impurities were concentrated. Zone melting the eutectic with added 2,3-benzofluorene gave effective segregation of the latter.

Zone melting the anthracene/benzoic acid eutectic with added carbazole showed that k_{eff} for the latter is 0.6, which is considerably lower than the values measured for the anthracene/carbazole system alone.

1. Introduction

In 1956, Clar and Zander reported that the previously observed phosphorescence of tetracene in fact resulted from the presence of 5,12-tetracenequinone, and that purified, synthetic tetracene shows no phosphorescence.[1] Since that time, spectroscopic properties of tetracene have been reported in scores of publications, but little effort seems to have been devoted to characterizing the kinds and amounts of impurity in the research samples.

Tetracene is hard to purify: because of its sensitivity to light and oxygen, it cannot readily be purified by displacement chromatography. Its thermal instability precludes zone melting. For these reasons, we have investigated the purification of tetracene by two

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techniques which can be carried out in the absence of oxygen, in total darkness, at temperatures well below the melting point.

2. Vapor Zone Refining

The first of these is a vapor-solid analog of zone melting which has been called vapor zone refining.[2,3] The process may be understood in terms of a composition-temperature plot for a mixture of compounds A and B at constant pressure (Fig. 1). If vapor of composi-

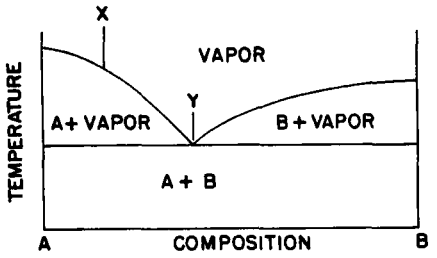

Figure 1. Solid vapor phase diagram (constant pressure).

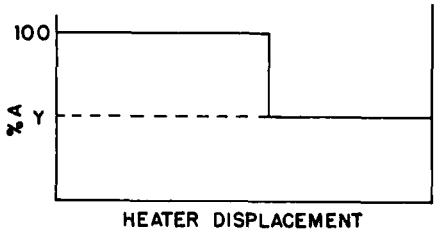

Figure 2. Segregation by vapor zone refining.

tion X is cooled, solid A will form and the remaining vapor will become correspondingly richer in B. When the composition of the vapor reaches Y, the solid formed also has this composition and the remainder of the vapor will give condensate of this constant composition. Figure 2 shows the concentration profile which would result from passage of a zone of vapor through a bar of solid mixture showing such a phase diagram. In a succeeding passage, no change of concentration would take place until the zone reached the discontinuity. At this point, the vapor would again contain some B, but the condensing solid would consist of pure A. Additional zone

passages displace the discontinuity to the right. The fundamental advantage of this procedure is that it makes sublimation iterative, in much the same way that zone melting makes directional freezing iterative.

3. Eutectic Zone Melting

One of the severest limitations to the broader use of zone refining for purification of organic chemicals is the decomposition that accompanies the melting of many organics. It is possible to subject a chemical to solid/liquid transition at a temperature below its melting point by combining it with another substance. If a liquid mixture is of eutectic composition, the solid that forms from it will have the same composition. Hence, solidification of a binary eutectic results in no change of composition.

If one of the components of the eutectic mixture contains an impurity, there is the possibility that solidification of the eutectic will result in segregation of the impurity. The *a priori* likelihood of such segregation is enhanced by the high degree of crystal perfection that is expected to result from solidification of a lamellar eutectic.[4]

In 1958, Sue and his coworkers reported the zone melting of eutectic mixtures of inorganic salts with water.[5] In such systems, they were able to separate sodium nitrate from potassium nitrate and cesium nitrate from sodium nitrate. More recently, Mokhosoev and his coworkers reported the purification of calcium nitrate[6] by zone melting the calcium nitrate/potassium nitrate eutectic. Surprisingly, this technique has not yet been applied to organic systems.

The essential requirements for effective eutectic zoning are that the second component (1) form a thermally stable, non-reactive mixture with the substance to be purified, with a melting point well below that of the compound of interest; (2) give segregation coefficients that are less than unity for impurities; (3) be readily available; (4) be readily removable from the mixture; and (5) give a eutectic containing a high concentration of the compound of interest.

It has been observed that liquid mixtures of eutectic composition can solidify in several modes. It appears that the " normal " mode gives a solid of lamellar morphology, in which both phases are continuous. In the presence of an impurity, the lamellar morphology

degenerates to a colony structure which is also continuous, in the sense that neither phase is required to renucleate periodically, following cessation of growth of that phase.[4] It is to be expected that a continuous mode would provide more effective segregation of impurities than a discontinuous mode, since in the latter, high instantaneous growth rates occur and impurities may be trapped in rapidly solidifying melt.

Eutectic zoning may be applicable to problems other than thermal instability. For example, materials with very high vapor pressure at their melting points might be purified as eutectics, at lower temperatures.

It should be mentioned that zone refining of multi-component organic mixtures has been discussed. Pfann has outlined the principles of " Zone Chromatography " in which relatively small amounts of mixed substances are applied to a bed of a matrix material and caused to traverse the bed in a molten zone.[7] Separation is achieved if the matrix material gives different distribution coefficients with each component of the applied mixture. This approach was applied to polymer fractionation by Peaker and Robb and by Loconti, who applied polystyrenes to columns of naphthalene and benzene respectively.[8,9]

To test the effectiveness of eutectic zoning in organic systems, we sought to apply it to a known separation problem, viz., the removal of carbazole from anthracene. Although anthracene is stable at its melting point and can be zone melted, the separation of carbazole is not trivial since the effective distribution coefficient of carbazole in anthracene is close to unity. The purification of tetracene poses a more difficult problem, since it decomposes rapidly at its melting point. For this reason, eutectic zoning was applied so that its effectiveness could be compared with sublimation.

4. Experimental Section

(I) Construction of a Vapor Zone Refiner

Figure 3 shows an all-glass vapor zone refiner. Heater A moves over the tube, traversing compacted ingot B, which is confined between discs C of Teflon®† fluorocarbon resin; these are moved by

† Du Pont Registered Trademark.

means of stainless-steel shafts E passing through plugs D of Teflon® which contain internal O-rings to seal rods E. In use, this device was inconvenient for three reasons: the entire apparatus had to be handled during loading; the heater had to be installed permanently

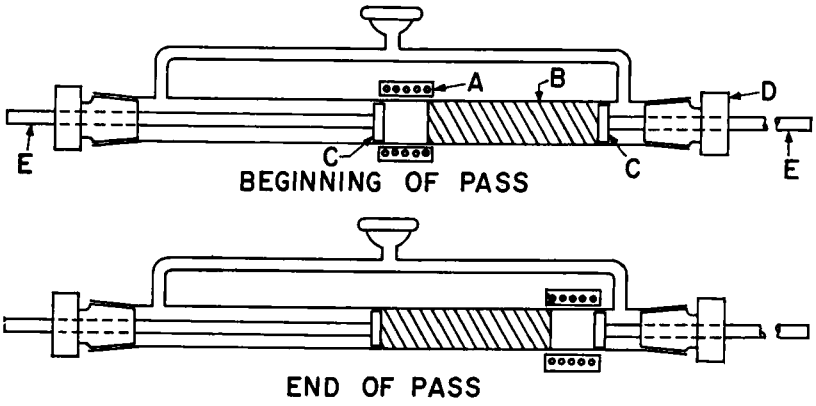

Figure 3. Vapor zone refining

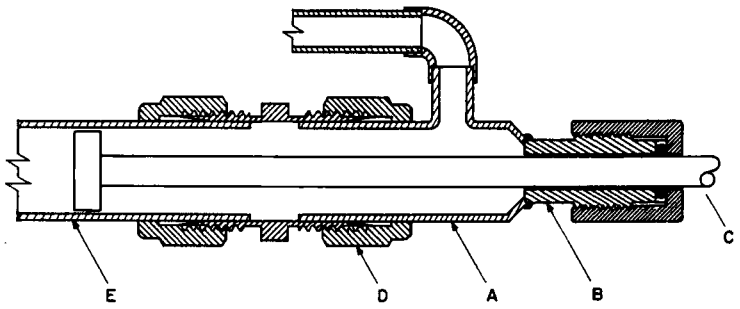

Figure 4. Metal vacuum apparatus for vapor zone refining.

in the closed loop formed by the vacuum side-arm; and the refined product had to be removed very cautiously to avoid breakage. A new unit was built in which the sample is contained in a length of glass tubing coupled to a metal evacuation yoke. One end of the yoke is shown in Fig. 4. A brass tee tube A, of $\frac{3}{4}$-in. OD, was brazed to O-ring coupling B (Vacuum Electronics Corp., Cat. No. C–25) which seals shaft C. Part D is a Swagelok union fitting (Crawford

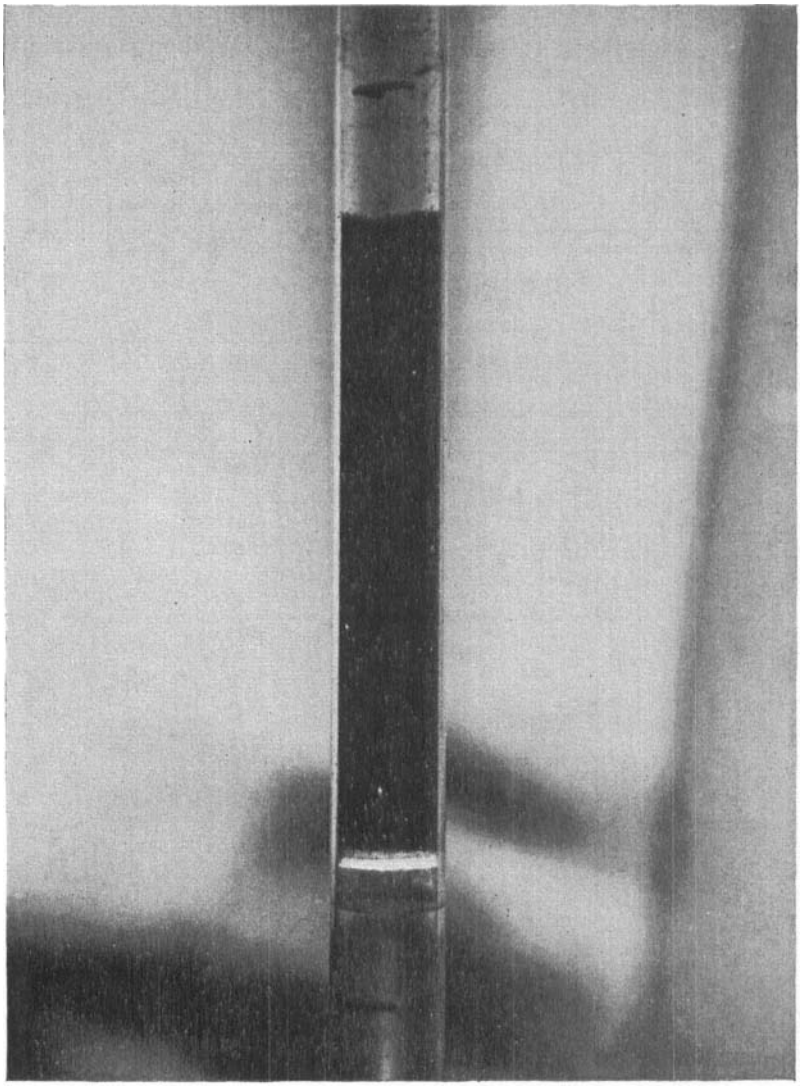

Figure 5.

Fitting Co., Part No. 1210–6) modified to allow free passage of the 19-mm. Pyrex tube E(19 mm OD × 50 cm long) through its entire length. The side port of each tee tube is connected to a vacuum system. It is necessary that parts A and B at both ends of the assembly be accurately colinear.

(II) Purification of Tetracene by Vapor Zone Refining

A 19-mm OD tube was charged with a firmly compacted 18-cm column of tetracene (21 gm, Rüttgerswerke). A 50-watt heater, 2.5 cm long, was positioned on the tube, and a double-ferrule union was slipped onto each end. The loaded tube was placed in its evacuation yoke, and the unions were slipped outward and tightened, to connect with the yoke. After the stainless-steel shafts bearing confining discs of Teflon® were positioned and sealed, the system was evacuated to ca. 10^{-5} torr and the heater at 200 °C was moved over the charge at 6 mm. per hr. After completion of each pass, the confining discs of Teflon® were repositioned and a new pass was begun, starting at the void between the disc and the head of the ingot. After 12 passes, the ingot showed a narrow, bright yellow band at the start, and was otherwise uniformly orange. In ultraviolet light (365 nm), the yellow band showed strong, yellow fluorescence while the remainder of the ingot showed none (Fig. 5).

(III) Characterization of Impurities from Tetracene

A. The yellow fluorescent material was removed and sublimed in vacuum through a gradient heater[10] at a maximum temperature of 250 °C. A small amount of tetracene (m.p. 344–349 °C) was recovered from the hot end of the tube; the cold end of the tube gave 1.4 gm of light-yellow crystals melting at 198–206 °C. A 1-mg sample of this solid was injected into a gas chromatograph and the emerging peaks were trapped in Pyrex tubes loosely packed with purified glass wool. The condensed fractions were washed from the glass wool with 2,2,4-trimethylpentane directly into quartz cells for measurement of their UV-absorption spectra. The properties of the chromatographic fractions and the assignments based on the spectra are summarized in Table 1.

Table 1. Gas Chromatography† of Impurities from Tetracene

Cut	Time (min)	Area %	Color of condensate	Fluorescence	Assignment
1	10–13	1	not visible	blue	anthracene
2	21–23	30	white	yellow	2,3-benzofluorene
3	23–31	33	pale yellow	yellow-green	pyrene
4	31–37	36	yellow	yellow-green	chrysene
5	37–45		red-orange	weak orange	tetracene

† Burrell-KD chromatograph; 2 ft × ¼ in. OD stainless steel column, 10% Apiezon L on 60–80 mesh Gas-Chrom Z. Inlet and detector 280 °C; Column temperature 100 to 250 °C at 20 °C/min, then isothermal at 250 °C.

B. A 1-gm sample of the impurity fraction isolated in (III)A was dissolved in benzene and extracted successively with dilute hydrochloric acid and dilute sodium hydroxide. The aqueous extracts were respectively alkalized and acidified, then back-extracted with ether. The ether solutions gave 7.0 and 10.4 mg, respectively, of basic and acidic impurities.

C. It is possible that the impurities described in Table 1 are not the only ones present in the original sample: others might have decomposed in the column, failed to elute, or remained unresolved. To learn whether other compounds are present, samples of the neutral (extracted) fraction from (III)B were introduced into a mass spectrometer (Du Pont Model CEC–21–110B) and masses of major parent ions were measured by peak-matching with appropriate peaks of a perfluorokerosene reference. The measured masses are tabulated in Table 2, along with masses calculated for the most probable empirical formulas.

Figure 6a shows a chromatogram obtained from this mixture in a high-resolution liquid chromatograph (Du Pont LC 820–0116), under the following operating conditions:

Column: " Permaphase " ODS (octadecylsilane), 1 m × 2.1 mm ID

Solvent: methanol-dimethylsulfoxide, 4 : 1

Sample: 2.0 μg/2.0 μl
Mobile Phase: 55% methanol/45% water (v/v)
Column Temperature: 60 °C
Column Pressure: 1100 psig
Flow Rate: 1.2 ml/min
Detector: UV photometer at 254 nm

TABLE 2 High-Resolution Mass Spectroscopy of a Neutral Impurity Fraction from Tetracene

Observed m/e	Calculated m/e	Empirical formula
216.0940	216.0939	$C_{17}H_{12}$
218.0738	218.0732	$C_{16}H_{10}O$
226.0786	226.0783	$C_{18}H_{10}$
228.0950	228.0939	$C_{18}H_{12}$
230.0744	230.0732	$C_{17}H_{10}O$
230.1105	230.1095	$C_{18}H_{14}$
232.0900	232.0888	$C_{17}H_{12}O$
232.1241	232.1252	$C_{18}H_{16}$
234.0510	234.0505	$C_{16}H_{10}S$
244.0902	244.0888	$C_{18}H_{12}O$
246.1051	246.1045	$C_{18}H_{14}O$

The solution was allowed to stand for several days in darkness, but in the presence of air. Figure 7a shows the chromatogram of the aged solution. Peak 2, at 1.8 min. retention, appears clearly in Fig. 7a, but only as a shoulder of peak 1 in Fig. 6a. Peaks 3, 4, 5, 9, 10, and 11 are likewise more readily seen in Fig. 7a than in Fig. 6a, while peak 12 is missing from the chromatogram of the aged solution. Peaks 6 and 7 grew with aging, and peak 14 diminished. It should be noted that while *changes* in peak size are significant, the sizes of the peaks do not necessarily reflect the relative abundances of the components of the mixture, since the recorder response depends on the intensity of light absorption at 254 nm.

The same mixture was chromatographed with gradient elution, during which the mobile phase was changed linearly from 20% methanol in water to 100% methanol, at 2% per min. Figure 6b shows the enhanced resolution afforded by this procedure. Similarly, Fig. 7b shows a gradient elution chromatogram of an aged solution.

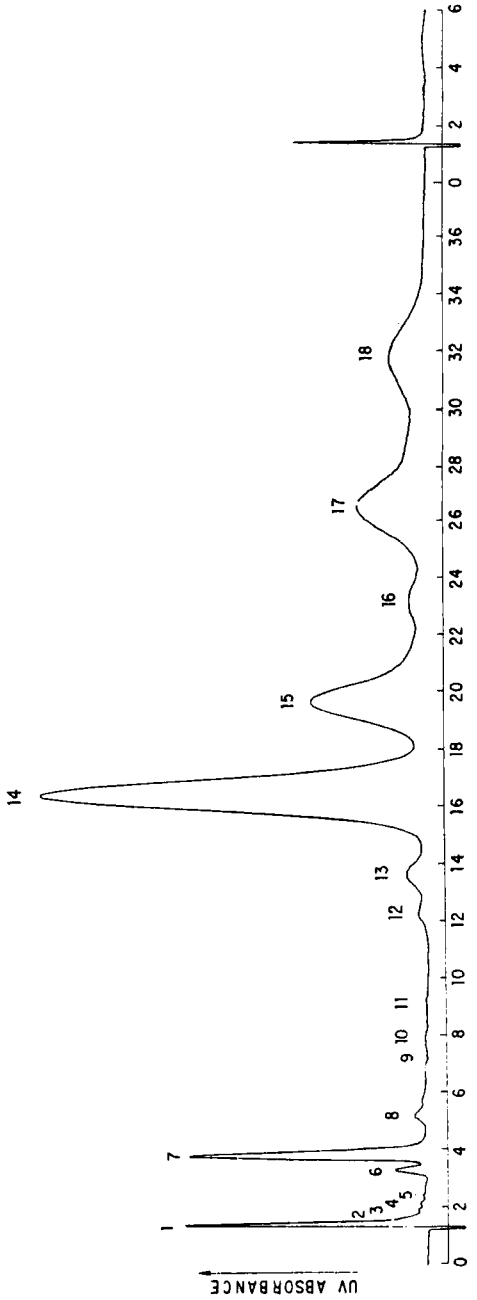

Figure 6a. Liquid chromatography of impurities from tetracene-freshly prepared solution.

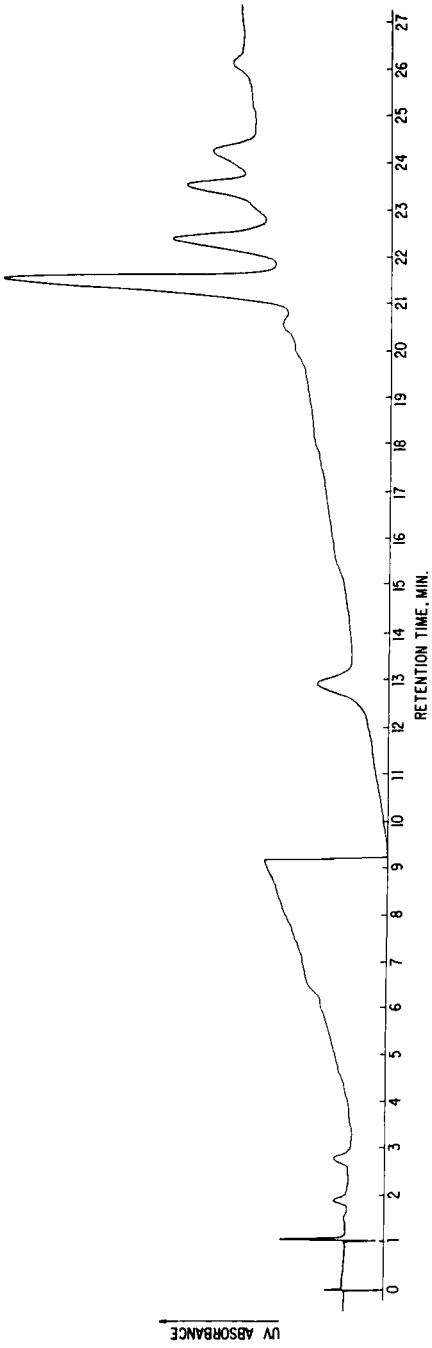

Figure 6b. Gradient elution liquid chromatography of impurities from tetracene-freshly prepared solution.

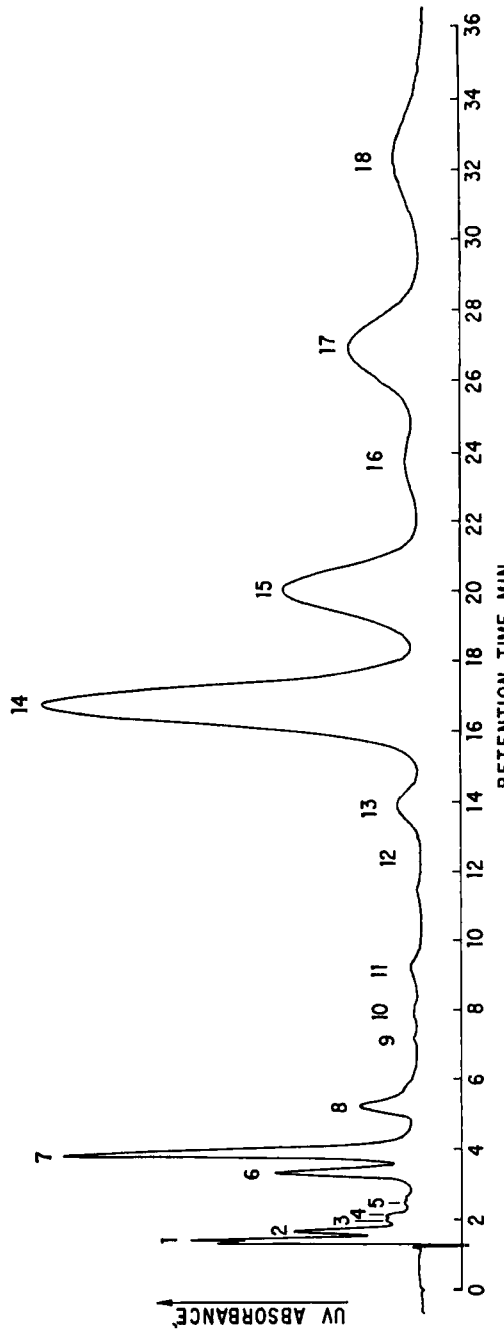

Figure 7a. Liquid chromatography of impurities from tetracene-aged solution.

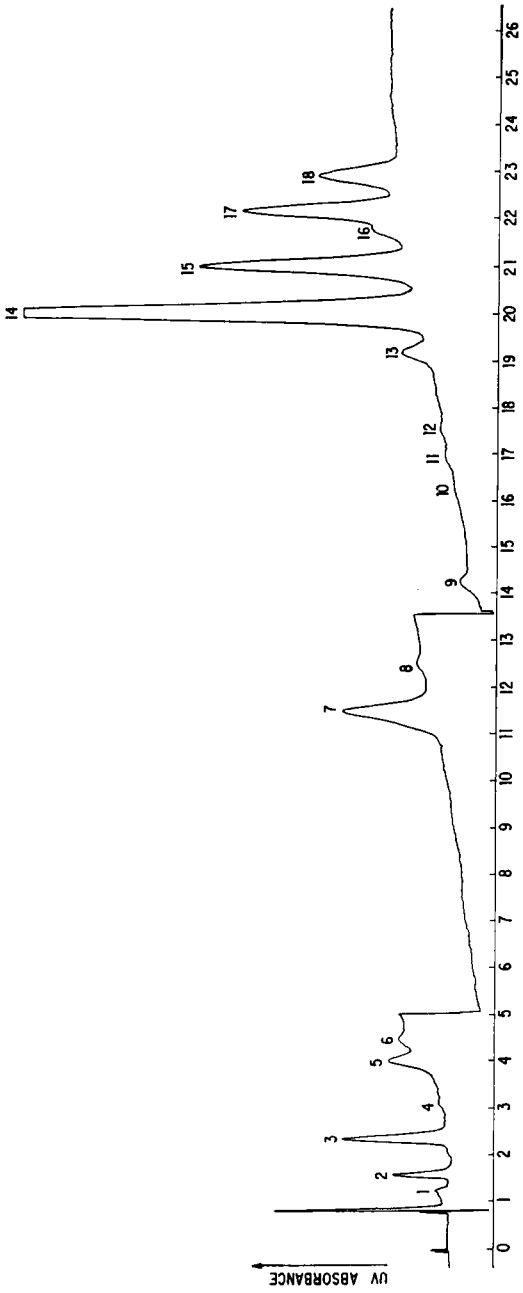

Figure 7b. Gradient elution liquid chromatography of impurities from tetracene-aged solution.

Both Figs. 6b and 7b show increases in " early " components. Since increased solute polarity results in decreased retention on the ODS column, it seems likely that oxidation of hydrocarbons to ketones or quinones is responsible. In fact, a freshly prepared solution of authentic 2,3-benzofluorene gave a single, sharp peak at 20.0 min. when chromatographed with gradient elution; after standing in darkness for two days, it still gave one peak, but after an additional two days in room light, a new peak appeared at 12.3 min. In like manner, anthracene (which eluted at 16.8 min) gave rise to a new peak at 4.4 min, which is the retention time of authentic anthraquinone.

TABLE 3 Assignment of Peaks in the Chromatograms of Tetracene Impurities

Fig. 7a Retention peak Time, Min.	No.	Fig. 7b Retention peak Time, Min.	No.	Assignment	Empirical formula
1.4	1	1.2	1		
1.8	2	1.6	2		
2.0	3	2.4	3		
2.1	4	3.1	4		
2.6	5	4.0	5	4,5-iminophenanthrene	$C_{14}H_9N$
3.4	6	4.4	6	anthraquinone	$C_{14}H_8O_2$
4.0	7	11.5	7	5,12-tetracenequinone	$C_{18}H_{10}O_2$
5.3	8	12.5	8	2,3-benzofluorene-9-one	$C_{17}H_{10}O$
7.2	9	14.2	9		
8.0	10	16.2	10		
9.2	11	16.9	11	anthracene	$C_{14}H_{10}$
12.3	12	17.5	12		
13.8	13	19.2	13	brasan	$C_{16}H_{10}O$
16.6	14	20.0	14	2,3-benzofluorene 5,12-dihydrotetracene	$C_{17}H_{12}$ $C_{18}H_{14}$
19.7	15	21.0	15	chrysene 1-methylpyrene	$C_{18}H_{12}$ $C_{17}H_{12}$
23.3	16	21.8	16	1,2-benzodiphenylene sulfide	$C_{16}H_{10}S$
26.4	17	22.2	17	tetracene	$C_{18}H_{12}$
32.3	18	—	18		

Similarly, it was established that phenanthrene, 1,2-benzanthracene, and fluorene are *not* present in the mixture.

Compounds having the empirical formulas shown in Table 2 were chromatographed and then added to the mixture of impurities. By noting coincidences of retention time, the assignments given in Table 3 were made.

(IV) Eutectic Zone Melting

A. *Anthracene/Benzoic Acid*

1. Establishment of Eutectic Composition. Mixtures of anthracene and benzoic acid were prepared at a number of concentrations and their melting ranges were determined by visual observation in capillaries. Mixtures containing 10–70% anthracene showed onset of melting at about 117 °C. A 10% anthracene/benzoic acid mixture melted at 117–119.4°, indicating that the eutectic composition is near this value.

A mixture of 8.5 g of benzoic acid and 1.5 g of anthracene was charged into a zone-melting tube 11 mm OD × 20 cm long. The resulting 13-cm ingot was subjected to 6 zone passes at 25 mm per hr. It was then sectioned and analyzed by gas chromatography (Column: 6 ft × ¼ in. OD stainless steel, 10% UCW-98 on Gas-Chrom Z. Temperatures: Column 215 °C, inlet 300 °C and detector 200 °C). The concentration of anthracene was nearly constant throughout the ingot.

2. Eutectic Zone Melting of Anthracene Containing Carbazole. A mixture of 1.5 g of anthracene and 8.5 g of benzoic acid with 16 mg of tritiated carbazole (general label; specific activity 4.2×10^{-7} dpm per mg.) was charged into an 11 mm OD × 20 cm zone-melting tube[11] and the resulting ingot was subjected to 6 zone passes at 25 mm per hr. It was then sectioned, radioactivity was measured by scintillation counting, and the anthracene/benzoic acid ratio was determined as before. The concentration of carbazole-T in anthracene was calculated for each point. Results are shown in Fig. 8. This figure also shows curves computed for $k = 0.5$ and $k = 0.7$, with geometrical factors similar to those used in this experiment[12].

In an experiment similar to that described above, 5 mg of carbazole-T in a mixture of 0.75 g of anthracene with 7.5 g of benzoic acid was subjected to 25 zone passes and analyzed as before except that no separate chromatographic analysis was made for the anthracene/benzoic acid ratio. The resulting data are shown in Fig. 9 along with theoretical curves for 20 passes with $k = 0.5$ and 0.7.

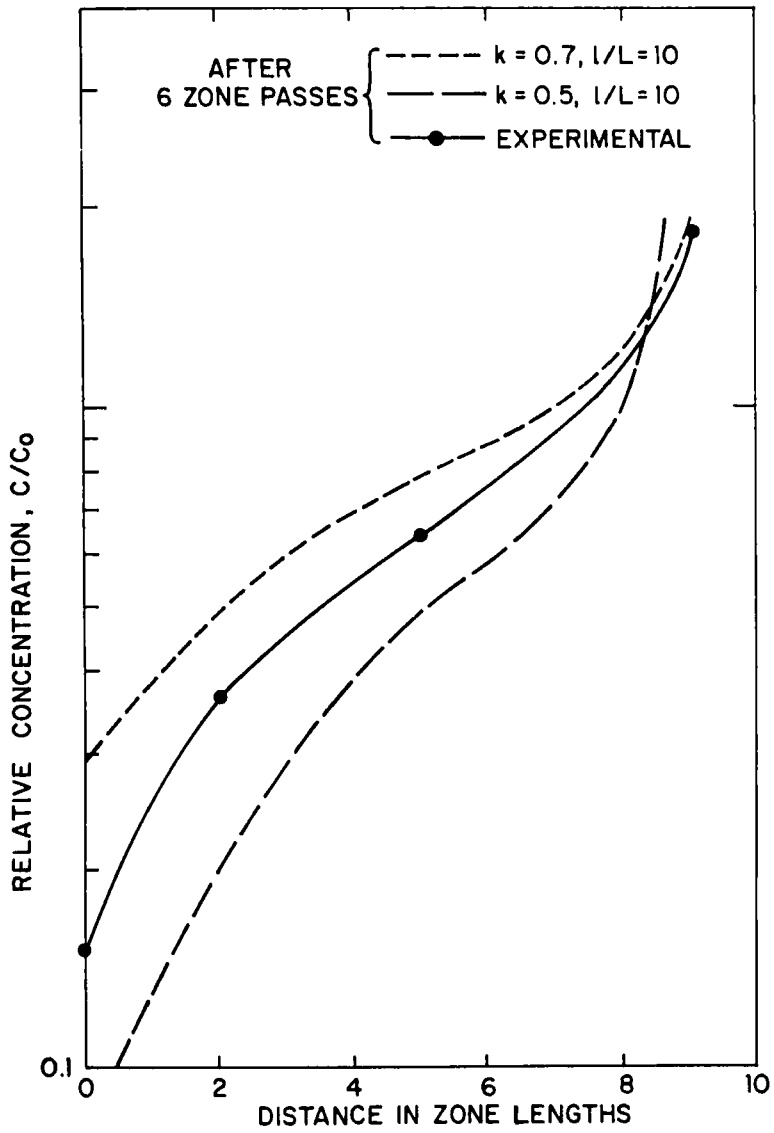

Figure 8. Segregation of carbazole from anthracene/benzoic acid.

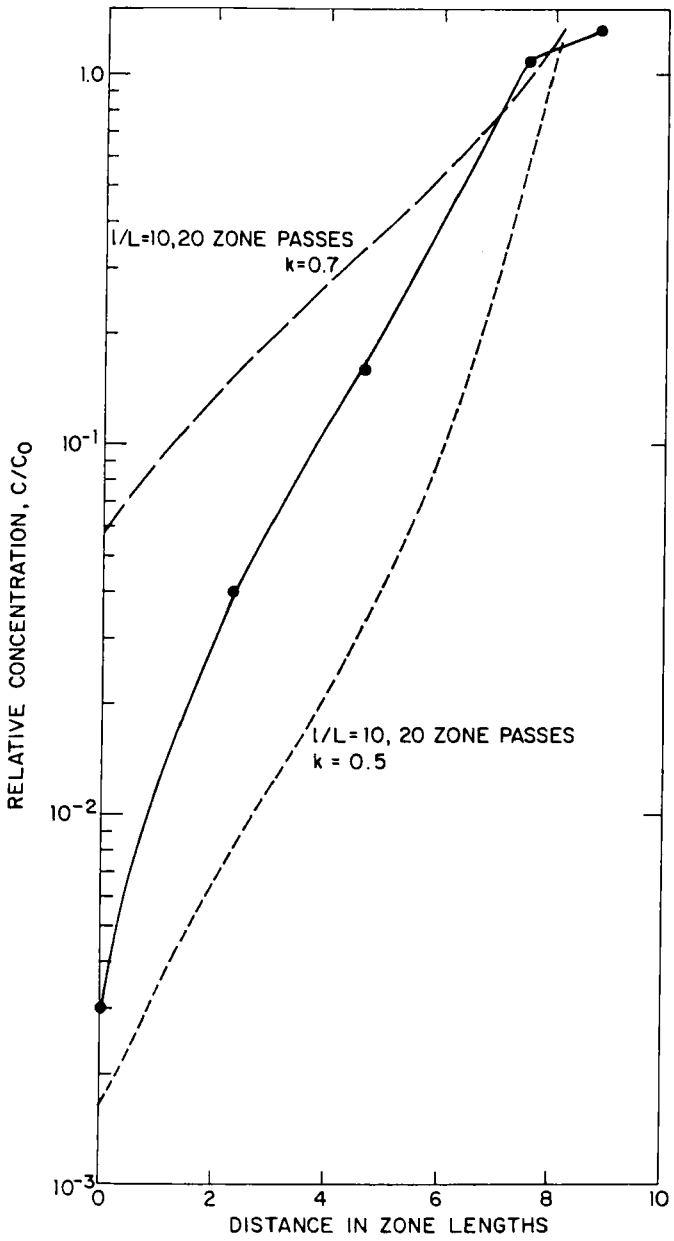

Figure 9. Segregation of carbazole from anthracene/benzoic acid.

B. *Tetracene/2-Naphthoic Acid*

1. Establishment of Eutectic Composition

(a) Tetracene and 2-naphthoic acid were charged into an 8-mm. OD × 40 cm. zone-melting tube. The mixture was held above the melting point of naphthoic acid and agitated until the acid was saturated with tetracene. The solidified ingot was subjected to 25 zone passes, then sectioned and analyzed colorimetrically for tetracene (Bausch and Lomb Spectronic 20) using 475 nm. light. The lower half of the ingot contained about 7 wt. % tetracene.

(b) A mixture of 1 g. of tetracene (Henley, Reagent Grade) plus 12 g. of 2-naphthoic acid (J. T. Baker Chemical Co., resublimed) was charged into a 9 mm. OD zone-melting tube and subjected to 30 zone-melting passes. The ingot was sectioned and analyzed by gas chromatography. The uppermost 2/3 of the ingot had a fairly uniform concentration of about 7 wt. % tetracene.

2. Eutectic Zone Melting of Tetracene Containing 2,3-Benzofluorene. A 9 mm OD zone-melting tube was charged with 1 g of tetracene, 12 g of 2-naphthoic acid, and 20 mg of 2,3-benzofluorene (Henley, Reagent Grade). The mixture was subjected to 25 downward zone passes at 25 mm per hr. and the ingot was sectioned and analyzed by liquid chromatography. Sections 1 thru 6 gave elution curves like that in Fig. 10 while Section 7 (bottom) gave the elution curve shown in Fig. 11. Chromatographic experiments with known amounts of 2,3-benzofluorene added to tetracene showed that the minimum amount detectable was ca. 10^{-3} μgm in a 2 μgm sample. Thus the concentration of 2,3-benzofluorene was reduced from 2% to less than 0.05% in most of the ingot.

5. Conclusions

Vapor zone refining has shown that a typical batch of tetracene of coal-tar origin contains about 6% impurity, and analysis of the concentrated impurity fraction shows that it contains many structurally related hydrocarbons and heterocyclics. Further experiments show that zone melting eutectic mixtures of organic compounds is an effective purification technique. It is applicable to materials that are unstable or stable at their melting points and offers the possibility

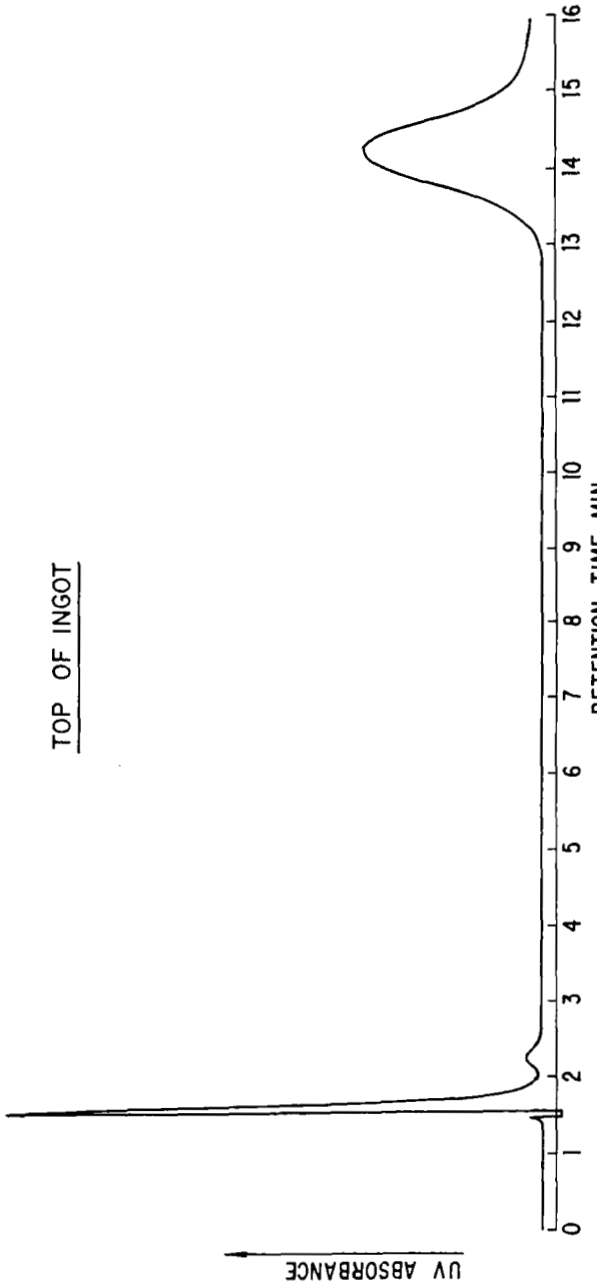

Figure 10. Liquid chromatography of eutectic zoned tetracene/2,3- benzofluorene.

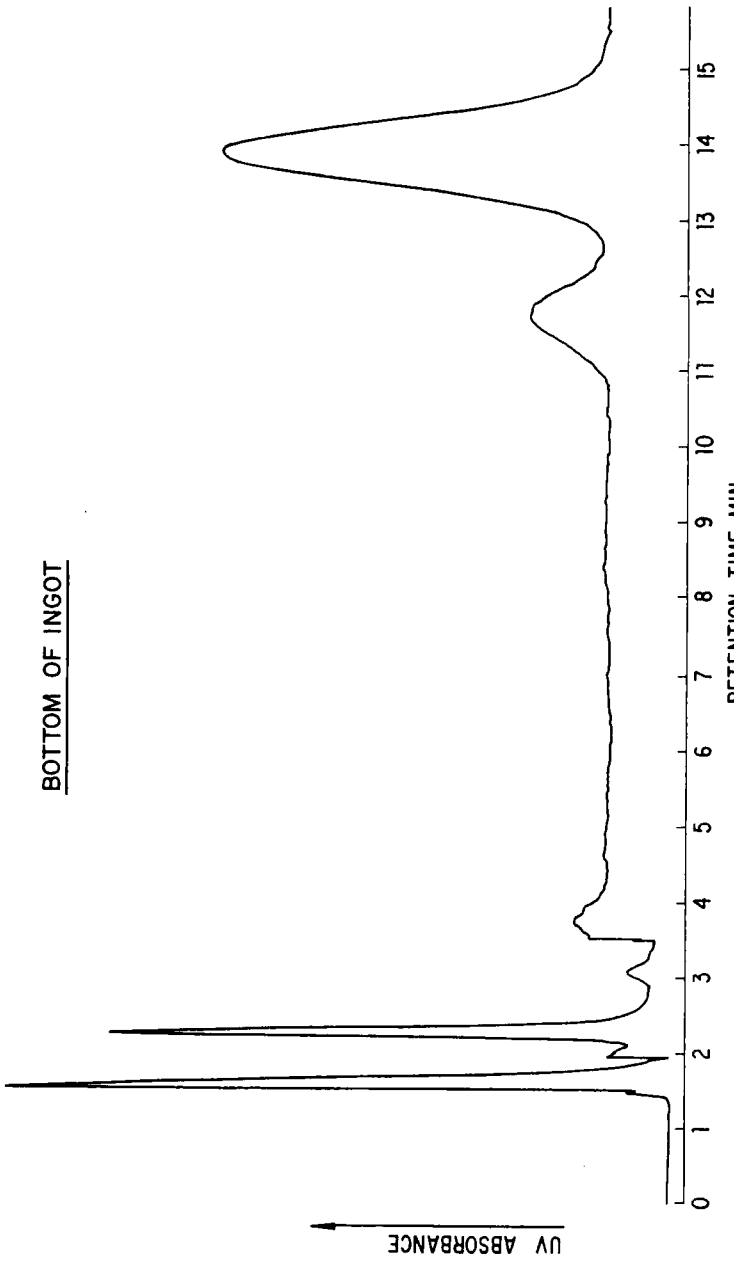

Figure 11. Liquid chromatography of eutectic zoned tetracene/2,3-benzofluorene.

of removing impurities whose effective distribution coefficients in conventional zone melting are close to unity. Thus in the case of anthracene/carbazole, both zone melting and normal freezing experiments at rather high concentrations indicate that K_{eff} is approximately 0.9. Results obtained in this work indicate that K_{eff} can be as low as 0.6 when C_0 is very low and the melt is agitated during growth. That a K_{eff} of 0.6 was attained in the eutectic zoning experiments must mean that the local conditions of crystallization in the eutectic mixture correspond to growth of a highly perfect crystal with concomitantly highly effective rejection of impurity.

Further, our results show that zone melting can be applied to a much broader range of organics than has been explored heretofore, since materials that melt with decomposition can be successfully zone melted, as components of eutectic mixtures. Tetracene is an almost classic case in that purification by crystallization from solvents is made difficult by its sensitivity to light and oxygen, and purification by sublimation is slow and not highly effective.

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