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CHROMATOGRAPHY OF AROMATIC HYDROCARBONS
ON IMPREGNATED LAYERS

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SUMMARY

Using silica gel layers impregnated with compounds having electron-acceptor properties, compared with non-impregnated layers a decrease in R_F values of aromatic hydrocarbons occurs when the same solvent is used. The R_F values do not correspond with the values of solid complexes of hydrocarbons with the relevant acceptors. They vary with the concentration of impregnating agents and, thus, are an indication of a modification in adsorption properties of the silica gel layer. The effect of impregnating layers when using a solvent of electron-acceptor properties is very limited. Chloranil and pyromellitic dianhydride form colored complexes with aromatic hydrocarbons and can be used for detection on impregnated layers with acceptor compounds which do not form colored complexes with the hydrocarbons.

INTRODUCTION

Aromatic hydrocarbons as donors of π electrons are capable of forming donor-acceptor complexes (EDA) with substances having electron-acceptor properties. This finding has been used by various authors for separation of polycyclic aromatic hydrocarbons on thin layers. Until now, the following methods have been used:

- (1) a plate already prepared is impregnated with a complex-forming agent;
- (2) a complex-forming agent is added to the adsorbent during preparation of the plate;
- (3) a plate already prepared without a complex-forming agent is developed in a system containing the complex-forming agent.

FRANCK-NEUMANN AND JÖSSANG¹ were the first to point out the possibility of using the EDA complexes in thin-layer chromatography. They separated polycyclic aromatic hydrocarbons on layers impregnated with *sym.*-trinitrobenzene, whereas polynitroaromatic substances were developed on non-impregnated layers in anthracene-containing systems. BERG AND LAM² added a small amount of complex-forming agent to the aluminium oxide and silica gel used as adsorbents. For separation of aromatic hydrocarbons, KESSLER AND MÜLLER³ used a saturated solution of picric acid as a developing system. Thin-layer chromatography was also used for the study of EDA

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complexes of other π donors, *e.g.* aromatic amines on layers impregnated with polynitroaromatic compounds⁴⁻⁶.

In the present study the effect is examined of impregnating commercially available silica gel plates with tetracyanoethylene and some acceptors from the group of halogen quinones, aromatic anhydrides, N-methylated cyclic ureids and bile acids, not yet used for separation of aromatic hydrocarbons. The study also included the caffeine previously examined². The polynitro substances as complex-forming agents were not studied here, since a considerable amount of work dealing with these substances already exists¹⁻⁶. As developing systems simple solvents with relatively clear-cut electron-acceptor (tetrachloroethylene) and electron-donor (di-*n*-butyl ether) properties were used.

EXPERIMENTAL

Chemicals

The origin and purity of the aromatic hydrocarbons studied and the methods used for their purification are listed in Table I. As solvents, predistilled di-*n*-butyl ether and tetrachloroethylene were used.

Tetramethyluric acid (TMUA) used for impregnation of the layers was prepared synthetically⁷. Caffeine PhBs 2, chloranil (Lachema p.a.) and tetracyanoethylene (TCNE, Lachema, pure) were purified by a repeated vacuum sublimation. Pyromellitic dianhydride (PMDA, Fluka, pure) and desoxycholate sodium (Léčiva Praha) were not purified prior to use.

TABLE I

AROMATIC HYDROCARBONS INVESTIGATED

| <i>Hydrocarbon</i> | <i>Origin</i> | <i>Purity</i> | <i>Purification method</i> |
|--------------------------|---------------------------|---------------|-------------------------------|
| Pentamethylbenzene | Synthetized after ref. 17 | | Crystallization from ethanol |
| Hexamethylbenzene | Synthetized after ref. 17 | | Crystallization from ethanol |
| 1-Methylnaphthalene | B.D.H. Great Britain | not given | — |
| 2-Methylnaphthalene | E. Merck | for synthesis | Distillation |
| 2,3-Dimethylnaphthalene | Koch-Light | purum | — |
| 2,6-Dimethylnaphthalene | Koch-Light | purum | — |
| Acenaphthene | Schering | purum | — |
| Acenaphthylene | B.D.H. Great Britain | not given | — |
| Fluorene | Loba-Chemie | purum | Recrystallization from xylene |
| 2,3-Benzofluorene | Schuchardt | purum | — |
| Fluoranthene | Schuchardt | not given | Crystallization from ethanol |
| 20-Methylcholanthrene | Koch-Light | purum | — |
| Biphenyl | Chemko, Strážske | not given | — |
| <i>m</i> -Terphenyl | Chemko, Strážske | not given | — |
| Anthracene | Lachema | for analysis | — |
| Phenanthrene | Lachema | | Zone refining |
| Chrysene | Loba-Chemie | purum | — |
| Pyrene | Koch-Light | purum | Sublimation |
| 3,4-Benzopyrene | Fluka | puriss. | — |
| 1,2,5,6-Dibenzanthracene | Koch-Light | purum | — |
| 1,2,3,4-Dibenzopyrene | Koch-Light | purum | — |
| 1,2,4,5-Dibenzopyrene | Koch-Light | purum | — |
| 3,4,9,10-Dibenzopyrene | Koch-Light | purum | — |
| Anthanthrene | Koch-Light | purum | — |

TABLE II
R_F VALUES OF AROMATIC HYDROCARBONS WITH VARIOUS ACCEPTORS

| No. | Hydrocarbon | Di- <i>n</i> -butyl ether | | Tetrachloroethylene | | | | | |
|-----|-------------------------|---------------------------|---------------------|---------------------|-----------------|-------------------------|---------------------|--------------------------|------|
| | | 0.05 M TMUA | Satd. solution TMUA | — | 0.05 M Caffeine | Satd. solution Caffeine | Satd. solution PMDA | Satd. solution chloranil | |
| 1 | Pentamethylbenzene | front | 0.96 | 0.90 | 0.74 | 0.76 | 0.84 | 0.74 | 0.72 |
| 2 | Hexamethylbenzene | front | 0.95 | 0.90 | 0.74 | 0.75 | 0.83 | 0.69 | 0.73 |
| 3 | 1-Methylnaphthalene | front | 0.85 | 0.75 | 0.73 | 0.73 | 0.76 | 0.71 | 0.76 |
| 4 | 2-Methylnaphthalene | front | 0.88 | 0.78 | 0.74 | 0.75 | 0.77 | 0.70 | 0.78 |
| 5 | 2,3-Dimethylnaphthalene | front | 0.83 | 0.67 | 0.75 | 0.74 | 0.74 | 0.60 | 0.67 |
| 6 | 2,6-Dimethylnaphthalene | front | 0.87 | 0.71 | 0.76 | 0.75 | 0.76 | 0.64 | 0.67 |
| 7 | Acenaphthene | front | 0.82 | 0.66 | 0.75 | 0.74 | 0.73 | 0.64 | 0.66 |
| 8 | Acenaphthylene | front | 0.72 | 0.52 | 0.70 | 0.69 | 0.63 | 0.46 | 0.62 |
| 9 | Fluorene | front | 0.80 | 0.65 | 0.68 | 0.69 | 0.66 | 0.61 | 0.60 |
| 10 | 2,3-Benzofluorene | 0.71 | 0.48 | 0.24 | 0.39 | 0.57 ^a | 0.11 ^a | 0.43 | 0.38 |
| 11 | Fluoranthene | 0.70 | 0.36 | 0.13 | 0.43 | 0.51 ^a | 0.13 ^a | 0.37 | 0.36 |
| 12 | 20-Methylcholanthrene | 0.68 | 0.32 | 0.11 | 0.39 | 0.53 ^a | 0.11 ^a | 0.34 | 0.35 |
| 13 | Biphenyl | front | 0.92 | 0.84 | 0.71 | 0.72 | 0.76 | 0.71 | 0.72 |
| 14 | <i>m</i> -Terphenyl | 0.94 | 0.89 | 0.77 | 0.62 | 0.62 | 0.69 | 0.68 | 0.64 |

^a In di-*n*-butyl ether.

TABLE III
R_F VALUES OF AROMATIC HYDROCARBONS WITH VARIOUS ACCEPTORS

| No. | Hydrocarbon | Di- <i>n</i> -butyl ether | | | Tetrachloroethylene | | | | |
|-----|--------------------------|---------------------------|----------------|---------------------------|---------------------|-------------------------------|------|---------------------------|--------------------------------|
| | | — | 0.05 M TMUA | Satd. solution TMUA | 0.05 M Caffeine | Satd. solution Caffeine | — | Satd. solution PMDA | Satd. solution chloranil |
| 1 | Anthracene | 0.69 | 0.49 | 0.26 | 0.55 | 0.42 | 0.45 | 0.46 | 0.46 |
| 2 | Phenanthrene | front | 0.68 | 0.44 | 0.66 ^a | 0.59 ^a | 0.71 | 0.51 | 0.60 |
| 3 | Chrysene | 0.67 | 0.32 | 0.12 | 0.47 | 0.27 | 0.40 | 0.36 | 0.37 |
| 4 | Pyrene | 0.70 | 0.34 | 0.13 | 0.51 | 0.32 | 0.46 | 0.36 | 0.43 |
| 5 | 3-4-Benzopyrene | 0.68 | 0.20 | 0.05 | 0.43 | 0.18 | 0.43 | 0.38 | 0.34 |
| 6 | 1.2.5.6-Dibenzanthracene | 0.68 | 0.28 | 0.07 | 0.44 | 0.21 | 0.37 | start | 0.32 |
| 7 | 1.2.3.4-Dibenzopyrene | 0.67 | 0.15 | 0.03 | 0.37 | 0.12 | 0.37 | 0.28 | 0.36 |
| 8 | 1.2.4.5-Dibenzopyrene | 0.65 | 0.12 | 0.03 | 0.34 | 0.10 | 0.39 | 0.26 | 0.34 |
| 9 | 3-4.9.10-Dibenzopyrene | 0.61 | 0.14 | 0.03 | 0.53 | 0.12 | 0.37 | 0.28 | 0.31 |
| 10 | Anthanthrene | 0.66 | 0.14 | 0.04 | 0.33 | 0.13 | 0.43 | 0.26 | 0.34 |

^a In tetrachloroethylene.

Chromatography

Benzene solutions of aromatic hydrocarbons (kept in darkness) were applied to 150×150 mm reflex silica gel foils Silufol (Kavalier, n.p.) without a luminescence indicator. Prior to use, the plates were impregnated by spraying as follows:

- (1) 0.05 *M* and saturated aqueous solution of TMUA;
- (2) 0.05 *M* and saturated aqueous solution of caffeine;
- (3) saturated solution of PMDA in ethyl acetate;
- (4) saturated solution of chloranil in chloroform;
- (5) 0.05 *M* aqueous solution of sodium desoxycholate;
- (6) 0.05 *M* TCNE solution in acetone.

After chromatography aromatic hydrocarbons were detected by spraying the plate with a saturated solution of chloranil in chloroform. The color of the spots could be intensified by heating the plates to about 110° . Substances No. 10-12, 15 and 17-24 could also be observed as fluorescent spots under UV light. For comparison of R_F values, solid complexes of pyrene with TMUA⁸, PMDA⁹ and TCNE¹⁰ have been prepared.

RESULTS AND DISCUSSION

Concentration of the acceptor compound in solution used for impregnation shows a marked effect on R_F values of aromatic hydrocarbons, as is evident from Tables II and III. These changes in R_F values are evidence of the altered adsorption properties of a layer, which behaves like a new type of adsorbent. The solid EDA complexes of pyrene listed under EXPERIMENTAL behave similarly to pyrene itself on non-impregnated layers. Due to the effect of solvent and adsorbent, a disintegration of the relatively weak donor-acceptor bond occurs⁴. As impregnating agents PMDA, chloranil, TMUA and caffeine, the last of these has been recommended², gave good results. When sodium desoxycholate was used, no effect was observed with aqueous solutions which were found suitable as mobile phase for separation by paper chromatography¹¹. R_F values of the aromatic hydrocarbons obtained on plates impregnated with tetracyanoethylene were not reproducible. TCNE is often used as a detection agent for aromatic compounds¹²⁻¹⁴, but later its limited effectiveness was reported¹⁵. On the layers impregnated with chloranil and PMDA lasting color stains are achieved after application of aromatic hydrocarbons (Table IV). For detection purposes, however, spots on plates impregnated with chloranil are more suitable; yellow-colored spots occurring mostly on plates impregnated with PMDA give less contrast when compared with spots on plates impregnated with chloranil.

The R_F values obtained on non-impregnated layers are influenced by the adsorption forces which increase, as a rule, with the number of aromatic rings in a molecule, regardless of their arrangement¹⁰. On layers impregnated with acceptor compounds, the situation is similar, since an increasing number of rings in a molecule of an aromatic hydrocarbon is also accompanied by a decrease in their ionization potential. The stability of the EDA bond is proportional to the difference between the electron affinity of the acceptor and the ionization potential of the donor.

The solvent has also a considerable effect on the quality of separation. Tetrachloroethylene causes considerably smaller differences than di-*n*-butyl ether in R_F values of aromatic hydrocarbons on both impregnated and non-impregnated plates;

TABLE IV

COLORS OF π COMPLEXES OF CHLORANIL AND PYROMELLITIC DIANHYDRIDE WITH AROMATIC HYDROCARBONS

| No. | Hydrocarbon | Color of π complex with chloranil | Color of π complex with PMDA |
|-----|--------------------------|---------------------------------------|----------------------------------|
| 1 | Pentamethylbenzene | brownish red | yellow |
| 2 | Hexamethylbenzene | reddish violet | light yellowish brown |
| 3 | 1-Methylnaphthalene | greyish brown | yellow |
| 4 | 2-Methylnaphthalene | brown | yellow |
| 5 | 2,3-Dimethylnaphthalene | brown | yellow |
| 6 | 2,6-Dimethylnaphthalene | grey | yellow |
| 7 | Acenaphthene | bluish grey | orange |
| 8 | Acenaphthylene | brown | yellow |
| 9 | Fluorene | brownish violet | yellow |
| 10 | 2,3-Benzofluorene | dark brownish grey | yellowish brown |
| 11 | Fluoranthene | brown | light yellow |
| 12 | 20-Methylcholanthrene | greenish yellow | grey |
| 13 | Biphenyl | yellowish brown | light yellow |
| 14 | <i>m</i> -Terphenyl | yellowish brown | light yellow |
| 15 | Anthracene | greenish blue | reddish pink |
| 16 | Phenanthrene | brown | yellow |
| 17 | Chrysene | brownish grey | yellowish brown |
| 18 | Pyrene | dark green | light red |
| 19 | 3,4-Benzopyrene | greenish yellow | grey |
| 20 | 1,2,5,6-Dibenzanthracene | grey | yellowish brown |
| 21 | 1,2,3,4-Dibenzopyrene | greenish yellow | yellowish brown |
| 22 | 1,2,4,5-Dibenzopyrene | greenish yellow | greyish brown |
| 23 | 3,4,9,10-Dibenzopyrene | greenish yellow | yellowish green |
| 24 | Anthanthrene | yellow | light green |

since with an excess of the acceptor solvent the effect of the complex-forming agent from the impregnated plate can only be shown to a lesser degree.

It is impossible to attain such a homogeneous distribution of the complex-forming agent on the plate by the spray-impregnation method as by the addition of the complex-forming agent to the adsorbent during preparation of the plates². A satisfactory reproducibility (R_F value ± 0.05), however, indicates that the former method is also suitable for practical separation of aromatic hydrocarbons.

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