

USE OF THE " π "-ELECTRON INTERACTION FOR SELECTIVE SEPARATION OF SOME QUINOLINE BASES, AND AROMATIC AND HETEROCYCLIC HYDROCARBONS FROM COAL TAR DISTILLATES BY GAS-LIQUID CHROMATOGRAPHY

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The selective sorption that is achieved when aromatic hydrocarbons are separated on stationary phases of aromatic character, is due to the ability of substances of similar structure to form association compounds. Paraffins may thus be readily separated from aromatics that have the same boiling range, e.g. cyclohexane from benzene etc.¹.

The substitution of an alkyl group in the aromatic ring causes steric hindrance of the association of these molecules, because the added group disturbs the regular spacing of the " π "-electron cloud. As regards the association of substances with similar structure (the one being the stationary phase, the other the compound chromatographed) the steric hindrance caused by the alkyl group has a greater effect on the chromatographic sorption (decrease of sorption) than the polarity due to the deformation of the " π "-electron arrangement on the nucleus. Thus, for instance, when separating polysubstituted biphenyls² an elution order was observed which corresponded mainly to the steric position of the methyl groups. Similarly, it is easier to separate ethylbenzene from *m*- and *p*-xylene than these two isomers from each other³.

If the stationary phases used are electron acceptors, then not only the sorption of the simple aromatic compounds is increased⁴, but for their alkyl derivatives that part of the total sorption ability that is due to the forces causing the deformation of the " π "-electron cloud, is also increased. The effect increases with increasing electronegativity and uniformity of the acceptor. LANGER *et al.*⁵ enhanced this effect by increasing the electronegativity of the carbonyl groups of phthalic acid esters, by introducing halogens on the nucleus. The influence of the deformation of the " π "-electron cloud is illustrated by the reverse order of elution of *m*- and *p*-xylene from di-*n*-propyl tetrachlorophthalate (see Table III).

Increased electronegativity may also be observed in the case of other electron acceptors, such as β, β' -oxydipropionitrile^{6,7}. ORR AND CALLEN⁸ (see also^{9,10}) used the esters of adipic acid with the same effect and achieved considerable selectivity in the separation of esters of fatty acids with one, two or more double bonds.

The fact that the same sorption effect occurs in the case of aromatic compounds and compounds with double bonds led us to investigate the possibility of using the donor-acceptor effect for the separation of some coal-tar substances containing

TABLE I
RETENTION DATA FOR QUINOLINE AND HIGHER PYRIDINE BASES AT 200°

| Compound | B.p. °C | Relative retention volumes | | |
|-----------------------------|------------|----------------------------|-----------|---------------|
| | | Reoplex 400 | Apieson L | Silicon E 301 |
| Quinoline | 238 | 1.00 | 1.00 | 1.00 |
| Isoquinoline | 243 | 1.18 | 1.14 | 1.15 |
| 2-Methylquinoline | 248 | 1.03 | 1.27 | 1.31 |
| 6-Methylquinoline | 258 | 1.36 | 1.54 | 1.53 |
| 7-Methylquinoline | 252 | 1.41 | 1.68 | 1.60 |
| 8-Methylquinoline | 248 | 0.98 | 1.39 | 1.40 |
| 1-Methylisoquinoline | 255 | 1.39 | 1.66 | — |
| 3-Methylisoquinoline | 251 | 1.19 | 1.57 | — |
| 2,4-Dimethylquinoline | 265 | 1.81 | 2.37 | 2.33 |
| 2,6-Dimethylquinoline | 267 | 1.50 | 2.14 | 2.06 |
| 2,4,6-Trimethylquinoline | 288 | 2.63 | 4.02 | 3.70 |
| 2,4,6-Trimethylpyridine | 170 | 0.14 | 0.23 | 0.037 |
| 2,3,5-Trimethylpyridine | 187 | 0.23 | 0.26 | 0.050 |
| 2,3,4-Trimethylpyridine | 192 | 0.30 | 0.48 | — |
| 2,3,5,6-Tetramethylpyridine | 130/100 mm | 0.38 | 0.51 | — |
| 2-Methyl-5-ethylpyridine | 175 | 0.17 | 0.29 | — |
| 4-Methyl-3-ethylpyridine | 196 | 0.26 | 0.46 | — |
| V_0^0 for quinoline | | 183 | 132 | 48 |

TABLE II
RETENTION DATA FOR SOME AROMATIC AND HETEROCYCLIC HYDROCARBONS AT 200°

| Compound | B.p. °C | Relative retention volumes | |
|-------------------------|---------|----------------------------|-----------|
| | | Reoplex 400 | Apieson L |
| Quinoline | 238 | 1.00 | 1.00 |
| Naphthalene | 218 | 0.54 | 0.82 |
| 2-Methylnaphthalene | 241 | 0.76 | 1.33 |
| 1-Methylnaphthalene | 243 | 0.87 | 1.46 |
| Indole | 253 | 3.20 | 0.97 |
| 2-Methylindole | 273 | 3.83 | 1.94 |
| 3-Methylindole | 266 | 3.71 | 1.89 |
| 5-Methylindole | 270 | 4.04 | 1.97 |
| 7-Methylindole | 268 | 3.57 | 1.79 |
| Biphenyl | 255 | 1.13 | 1.73 |
| 2,6-Dimethylnaphthalene | 261 | 1.06 | 2.18 |
| 1,6-Dimethylnaphthalene | 262 | 1.15 | 2.35 |
| 2,3-Dimethylnaphthalene | 265 | 1.33 | 2.42 |
| Acenaphthene | 278 | 1.75 | 3.20 |
| Diphenyl oxide | 287 | 2.52 | 3.50 |
| Fluorene | 295 | 3.10 | 4.83 |
| V_0^0 for quinoline | | 183 | 132 |

alkyl groups on the aromatic ring or the heteroatom, that cause deformations of the original " π "-electron arrangement.

EXPERIMENTAL

The measurements were carried out with an apparatus of Griffin & George, London, Type MK II with a millivoltmeter recorder (0-3 mV) of Honeywell-Brown. The column was packed with 20-30 % (w/w) substrate on Celite (Johns-Mansville C 545); hydrogen served as the carrier gas. 5-20 μ l samples were injected into the columns of approx. 80 cm length and 6-8 mm internal diameter. Detailed working conditions are reported at the respective places. Reoplex 400 (polyoxyalkylene adipate) was a product of Geigy & Co. Ltd., Manchester. Apiezon L Grease (Edwards High Vacuum Ltd.) and Silicon Elastomer E 301 were supplied by Messrs. Griffin & George, London.

The relative and absolute retention data are given in Tables I and II.

DISCUSSION

Table III shows the retention data of the characteristic model substances on various stationary liquids acting as electron acceptors.

The quantitative increase of the total selectivity to polar substances (carriers

TABLE III
COMPARISON OF SELECTIVITY OF SOME DONOR-ACCEPTOR TYPE BONDING STATIONARY PHASES

| Compound | B.p. °C | Relative retention volumes | | | | | |
|-------------------------|---------|--|---|---|---|---|--|
| | | Bis(ethyl-n-hexyl) sebacate (ref. ¹¹)* | Di-n-decyl phthalate (ref. ¹¹)* | Hexaethylene glycol dimethyl ether (ref. ⁷) | Di-n-propyl tetrachlorophthalate (ref. ⁸) | Polyoxyalkylene adipate (Reoplex 400) (found) | β,β' -Oxydi-propionitrile (ref. ⁷) |
| <i>Temperature 70°</i> | | | | | | | |
| Carbon tetrachloride | 76.7 | 0.90 | 0.89 | 0.70 | — | 0.59 | 0.36 |
| n-Heptane | 98.4 | 0.89 | 0.78 | 0.29 | — | 0.16 | 0.08 |
| Cyclohexane | 81.4 | 0.72 | 0.64 | 0.30 | — | 0.21 | 0.11 |
| Benzene | 80.1 | 1.00 | 1.00 | 1.00 | — | 1.00 | 1.00 |
| Ethylbenzene | 136.2 | 6.00 | 5.90 | — | — | 3.51 | 2.23 |
| <i>Temperature 110°</i> | | | | | | | |
| Benzene | 80.1 | 1.00 | 1.00 | — | 1.00 | 1.00 | 1.00 |
| Ethylbenzene | 136.2 | 4.35 | 4.4 | — | 3.05 | 2.82 | 2.36 |
| m-Xylene | 139.2 | 4.6 | 4.5 | — | 3.56 | 3.11 | } 2.61 |
| p-Xylene | 138.4 | 4.6 | 4.45 | — | 3.72 | 2.96 | |
| o-Xylene | 144.5 | 5.50 | 5.25 | — | 4.71 | 4.00 | 3.42 |
| n-Decane | 174 | 12.9 | 12.9 | — | 2.91 | 1.22 | 0.29 |
| Separation factors: | | | | | | | |
| o-Xylene/ethylbenzene | | 1.265 | 1.195 | — | 1.545 | 1.44 | 1.45 |
| m-Xylene/p-xylene | | — | — | — | 0.957 | 1.050 | — |

* Interpolated values.

of donors) may be pursued on the decreasing retention ratio of electroneutral compounds or compounds with an insignificant polarisation ability (*n*-decane, *n*-heptane, carbon tetrachloride). The type of forces that cause the total selectivity is, however, not uniform, as can be seen from the separation factors. The greatest effect is obtained with phases whose molecules accept the " π "-type electrons with only a single type of functional group. Though, for instance, polyoxyalkylene adipate or β,β' -oxydipropionitrile have higher total sorption activity, the participation of the " π "-electron interaction in these substances is lower due to the decrease of the effect of the $-\text{CO}-$ or $-\text{CN}$ acceptor-active functional groups in the molecule. For comparison the retention data are given of model substances on hexaethylene glycol dimethyl ether, of which the oxygen of the ether bonds also acts as an acceptor. This compound has a structure that is very similar to the alcoholic part of the adipate molecule.

Similar differences in the sorption selectivity may be expected also for higher aromatic hydrocarbons. In the case of quinoline bases the nitrogen, being a slight internal acceptor, acts mainly as a deformer of the " π "-electron cloud of the whole molecule. Evidence of this is given by the separation factors calculated from the observed data, which are summarized in Table IVa. A quantitatively higher selective effect may be observed in the case of diphenylene oxide, where the hetero-atom, a strong internal acceptor, causes permanent polarisation of the whole diphenylene oxide molecule. Such a permanent dipole causes the increased sorption (Table IVb). But only if the molecule of the chromatographed substance contains a functional group which acts as a donor of the available electron pair by itself, does the order of the sorption selectivity increase due to the formation of fragmental hydrogen bonds between the pyrrole nucleus and all the functional groups of the stationary phase; an example of such a compound is indole (Table IVc).

TABLE IV
COMPARISON OF SEPARATION FACTORS FOR SOME MODEL
COMPOUNDS ON APIEZON L AND REOPLEX 400
(Temperature 200°)

| Compounds | Separation factor | |
|---|-------------------|-------------|
| | Apiezion L | Reoplex 400 |
| (a) | | |
| 1-Methylnaphthalene/naphthalene | 1.78 | 1.62 |
| 1-Methylnaphthalene/2-methylnaphthalene | 1.10 | 1.15 |
| 2,3-Dimethylnaphthalene/1,6-dimethylnaphthalene | 1.03 | 1.16 |
| Isoquinoline/quinoline | 1.14 | 1.18 |
| 7-Methylquinoline/8-methylquinoline | 1.22 | 1.44 |
| Fluorene/acenaphthene | 1.51 | 1.77 |
| (b) | | |
| Fluorene/diphenylene oxide | 1.38 | 1.23 |
| (c) | | |
| Indole/quinoline | 0.97 | 3.20 |
| Indole/naphthalene | 1.18 | 5.93 |

In Figs. 1 and 2 examples of the selective separation possibilities are illustrated. The higher polyoxyalkylene adipates, in contrast to most of the substrates that show a similar effect, permit working temperatures above 200°, maintaining at the same

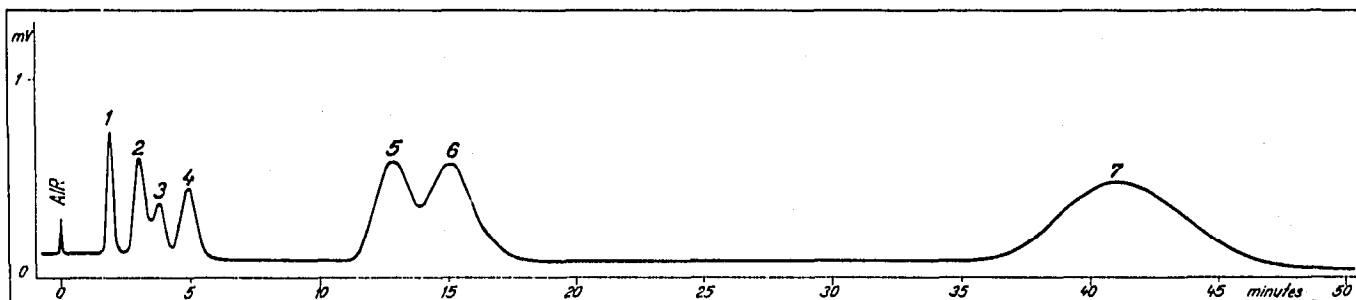


Fig. 1. Gas-chromatographic separation of some coal tar constituents containing nitrogen on Reoplex 400 at 200°. Column 0.7 × 88 cm; flow-rate 0.903 ml H₂/sec; inlet pressure 750 mm Hg; outlet pressure 250 mm Hg; 15.5 g packing containing 30% (w/w) substrate on Celite 545. Compounds: (1) 2,4,6-Trimethylpyridine. (2) 2,3,5-Trimethylpyridine. (3) 2,3,4-Trimethylpyridine. (4) 2,3,5,6-Tetramethylpyridine. (5) Quinoline. (6) Isoquinoline. (7) Indole.

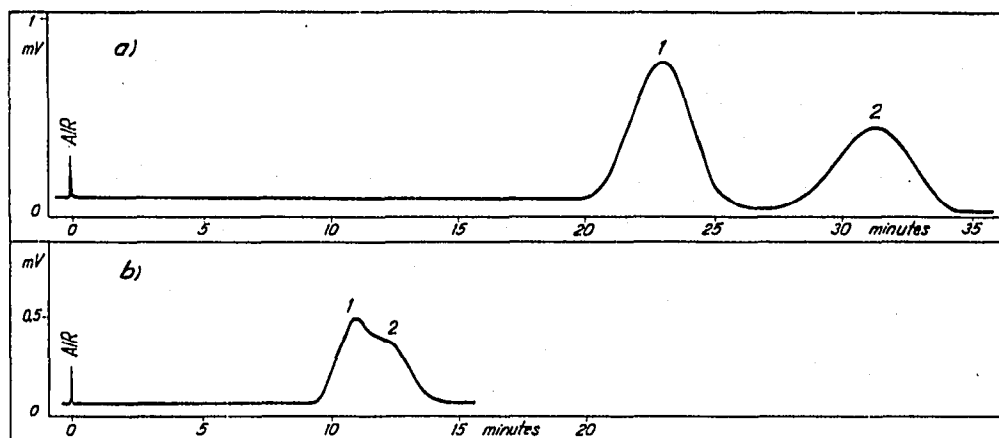


Fig. 2. Comparison of the separation of acenaphthene-diphenylene oxide on Reoplex 400 and on Apiezon L at 200°. (a) Column 0.7 × 88 cm; flow-rate 0.903 ml H₂/sec; inlet pressure 750 mm Hg; outlet pressure 250 mm Hg; 15.5 g packing containing 30% (w/w) Reoplex 400 on Celite 545. (b) Column 0.6 × 81 cm; flow-rate 0.833 ml H₂/sec; inlet pressure 756 mm Hg; outlet pressure 290 mm Hg; 7.9 g packing containing 20% (w/w) Apiezon L on Celite 545. Compounds: (1) Acenaphthene. (2) Diphenylene oxide.

time their high sorption selectivity. Therefore, they are suitable stationary phases for the analysis of higher boiling unsaturated compounds (terpenes and other hydrocarbons, alcohols, aldehydes, ketones, etc.) in mixtures with saturated compounds, and preferably for the separation of steric isomers of unsaturated substances.

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SUMMARY

The common principle of the donor-acceptor sorption interaction for a number of stationary phases was demonstrated.

Polyoxyalkylene adipate (Reoplex 400) was found to be a suitable stationary phase for the selective separation of quinoline bases, unsaturated, aromatic and heterocyclic compounds boiling up to 300°. At 200° the retention volumes of model substances were measured and verified by examples of suitable separation of substances from coal tar distillates.

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