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LIQUID CHROMATOGRAPHY OF HYDROCARBONS ON POROUS POLY-(ETHYLENE GLYCOL) METHACRYLATE (SPHERON P-300)*

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SUMMARY

The chromatographic behaviour of saturated, unsaturated and aromatic hydrocarbons on a macroporous bead copolymer of 2-hydroxyethyl methacrylate and ethylene dimethacrylate, with *n*-heptane as the mobile phase was studied, concentrating on the effect of the structure of the solute on its retention. The behaviour of conjugated unsaturated and aromatic hydrocarbons is in agreement with the theory of liquid-liquid chromatography; it is concluded that the chromatographic properties of the above system are better interpreted by using the separation mechanism of liquid-liquid chromatography than that of liquid-solid chromatography.

INTRODUCTION

Synthetic polymeric phases are applied in liquid chromatography not only as gel phases and ion exchangers, but also as sorbents. The phases most widely used in this respect have so far been chemically bonded phases, the matrix of which is formed by siloxane polymers¹. At the same time, however, the number of applications of polymeric packings in reversed-phase liquid chromatography (RPLC) has also increased, and only in normal-phase liquid chromatography (NPLC) has the use of polymeric packings remained somewhat stagnant.

The separation mechanism and the theory of the retention of the solute in adsorption liquid chromatography (LSC) on inorganic adsorbents have been examined by Snyder² in sufficient detail. The thermodynamic theory of the retention of the solute in liquid-liquid chromatography (LLC)³ and in RPLC⁴ has been worked out. There are different views about the mechanism of separation in sorption liquid chromatography on polymeric phases, including chemically bonded phases; systematic investigations of this problem and other practical information concerning the properties of polymeric materials have not yet provided a sufficient basis for a de-

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tailed description of the behaviour of these phases over the whole range of their uses⁵⁻⁸.

With bonded phases that possess the "brush" structure, the view that is almost unanimously accepted is that the separation mechanism consist in the adsorption of the solute molecules on the surface of a modified adsorbent⁸⁻¹². The adsorption mechanism has even been used to interpret the separation of polycyclic aromatic hydrocarbons on 1,2,3-tris(2-cyanoethoxy)propane coated on silica gel¹³. On the other hand, the mechanism of separation on polymeric bonded phases is explained both by adsorption^{7,11,12,14-19} and by partition^{7,12,14,15,19-25} in RPLC, and similarly by adsorption^{11,12,14,15} and by partition^{12,14-17,22} in NPLC.

Most practical data on the chromatographic behaviour of porous polymeric packings relates to gel chromatography, in which sorption is regarded as a side-effect; for this reason, these results are inadequate for a complete description of the separation mechanism in sorption liquid chromatography on such packings. In spite of this, however, the above effect is very frequently attributed to adsorption²⁶⁻³⁴, while partition^{35,36} or both effects³⁷⁻³⁹ are only rarely taken into account. Finally, it should also be pointed out that the results of work aimed directly at the sorption properties of porous polymeric packings in liquid chromatography are not uniform as regards the problem of the nature of the separation mechanism⁴⁰⁻⁴⁹. The behaviour of these packings is interpreted in terms of both LSC⁴²⁻⁴⁹ and LLC⁴⁰⁻⁴². It should be added, however, that the study of sorption chromatography on synthetic polymeric packings outside gel chromatography is almost exclusively restricted to styrene-divinylbenzene copolymers in RPLC⁴⁰⁻⁴⁸.

In this paper, the chromatographic behaviour of hydrocarbons on a macroporous copolymer of 2-hydroxyethyl methacrylate and ethylene dimethacrylate (Spheron P-300) in *n*-heptane is described, and relationships between the retention and structure of the solute and the separation mechanism of the system are discussed.

EXPERIMENTAL

Chemicals

All compounds were pure commercial samples and were used without further purification.

Liquid chromatography

The retention volumes were measured with a liquid chromatograph (120 × 0.8 cm column) and with an R 401 differential refractometer (Waters) as detector. The samples were injected as 1-5% solutions in *n*-heptane in volumes of 0.2 ml and characterized by the retention volume, V_R , in siphon counts (1 count = 1.81 ml). The adjusted retention volumes, V'_R , were calculated from the retention volumes by subtracting the dead column volume V_0 ; $V'_R = V_R - V_0$ ($V_0 = V_R$ for squalane). The column was packed with Spheron P-300 (Lachema, Brno, Czechoslovakia), exclusion limit $3 \cdot 10^5$, grain size 40-63 μm . The flow-rate of the mobile phase (*n*-heptane) was 1 ml/min.

RESULTS AND DISCUSSION

Table I gives the adjusted retention volumes of hydrocarbons that do not contain delocalized π -electrons. The retention volumes are so low that it is difficult to determine the character of this quantity as a function of some of the molecular parameters of the solute. A qualitative estimate of the order of elution indicates that retention is slightly reduced with increasing molecular weight, without any visible effect of branching of the hydrocarbon chain on this tendency. In addition, the retention is increased by the presence of the double bond and by the cyclic structure of the molecule of the solute.

TABLE I

ADJUSTED RETENTION VOLUMES OF LINEAR AND CYCLIC ALKANES AND LINEAR ALKENES ON SPHERON P-300 IN *n*-HEPTANE

<i>Compound</i>	<i>No. of carbon atoms</i>	V'_R	<i>Compound</i>	<i>No. of carbon atoms</i>	V'_R
Neohexane	6	1.7	<i>tert.</i> -Butylcyclohexane	10	1.7
<i>n</i> -Hexane	6	1.4	Cyclopentane	5	1.4
<i>n</i> -Octane	8	0.7	Cyclohexane	6	1.4
<i>n</i> -Decane	10	0.5	Decalin	10	1.1
2,2,4,6,6-Pentamethylheptane	12	0.5	Pentylcyclohexane	11	1.1
<i>n</i> -Dodecane	12	0.5	<i>tert.</i> -Pentylcyclohexane	11	1.0
<i>n</i> -Tetradecane	14	0.4	Tricyclohexylmethane	19	0.9
<i>n</i> -Pentadecane	15	0.4	1-Heptene	7	1.1
<i>n</i> -Tridecane	13	0.2	3-Heptene	7	1.1
<i>n</i> -Eicosane	20	0.2	1-Nonene	9	1.1
Squalane	30	0.0	1-Decene	10	0.9
Cycloheptane	7	2.0	1-Dodecene	12	0.8
Isopropylcyclohexane	9	1.9	1-Hexadecene	16	0.5

Table II gives the adjusted retention volumes of hydrocarbons that contain conjugated double bonds. If we call a certain type of the conjugated system a "functional group", then the values of the adjusted retention volumes of dienes, alkylbenzenes and alkylnaphthalenes form parallel straight lines for the individual functional groups in graphs of $\log V'_R$ versus the number of carbon atoms in the molecule (Fig. 1). If parallel straight lines are plotted through the points corresponding to the other compounds in Table II, the dependence obtained can be related to the empirical formula of the compound C_nH_{2n-z} . A similar type of dependence was obtained by Pierotti *et al.*⁵⁰ and Deal *et al.*⁵¹ for the extraction equilibria of hydrocarbons in systems of *n*-heptane with several polar solvents bearing a hydroxyl group, and by Stevenson⁵² in the LLC of alkylbenzenes in the system Carbowax 600-2,2,4-trimethylpentane. Such a correlation (Fig. 1) can, in terms of LLC, be regarded as the additivity of free energies^{50,51,53,54}:

$$\Delta G_t^E = n_i \Delta G^E(C) + (m_i - 1) \Delta G^E(X) + p_i \Delta G^E(Y) \quad (1)$$

where ΔG_t^E is a change in the excess free energy of the solute during sorption, n_i , m_i and p_i denote the number of carbon atoms, the number of double bonds in conjuga-

TABLE II

ADJUSTED RETENTION VOLUMES OF UNSATURATED CONJUGATED HYDROCARBONS ON SPHERON P-300 IN *n*-HEPTANE n (carbon number) and z are values determined by the empirical formula of compound C_nH_{2n-z} .

No. Compound	V'_R	n	z	No. Compound	V'_R	n	z
1 1,3-Butadiene	4.5	4	2	17 <i>p</i> -Cymene	4.3	10	6
2 1,3-Pentadiene	3.6	5	2	18 <i>sec.</i> -Butylbenzene	4.4	10	6
3 2-Methylbutadiene	3.5	5	2	19 Hexamethylbenzene	3.1	12	6
4 2,3-Dimethylbutadiene	3.0	6	2	20 <i>p</i> -Di- <i>tert.</i> -butylbenzene	1.9	14	6
5 1,3-Cyclooctadiene	3.1	8	4	21 Styrene	12.7	8	8
6 Benzene	9.4	6	6	22 Ethylstyrene	7.8	10	8
7 Toluene	7.9	7	6	23 Tetralin	7.0	10	8
8 Cycloheptatriene	7.8	7	6	24 Divinylbenzene	14.4	10	10
9 Ethylbenzene	6.4	8	6	25 Naphthalene	21.5	10	12
10 <i>o</i> -Xylene	6.9	8	6	26 1-Methylnaphthalene	16.3	11	12
11 <i>m</i> -Xylene	5.7	8	6	27 2-Methylnaphthalene	16.0	11	12
12 <i>p</i> -Xylene	5.4	8	6	28 2-Ethylnaphthalene	13.1	12	12
13 Cumene	5.5	9	6	29 2,3-Dimethylnaphthalene	14.5	12	12
14 1,2,3-Trimethylbenzene	6.4	9	6	30 Diphenyl	23.5	12	14
15 1,2,4-Trimethylbenzene	5.5	9	6	31 Anthracene	42.6	14	18
16 Mesitylene	4.5	9	6	32 Phenanthrene	43.8	14	18

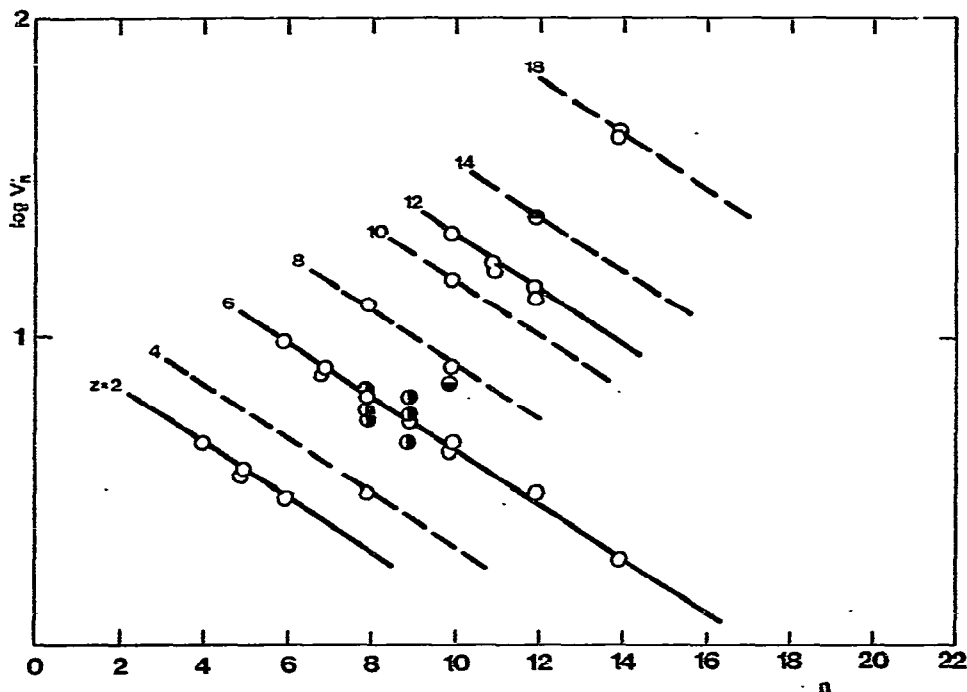


Fig. 1. Dependence of adjusted retention volumes (V'_R) of unsaturated hydrocarbons in Table II on the number of carbon atoms (n) for various z values of the empirical formula of compounds C_nH_{2n-z} on Spheron P-300 in *n*-heptane. Column, 120×0.8 cm; flow-rate of mobile phase, 1 ml/min. \circ , Isomeric di- and trimethylbenzenes; \bullet , tetralin; \ominus , diphenyl.

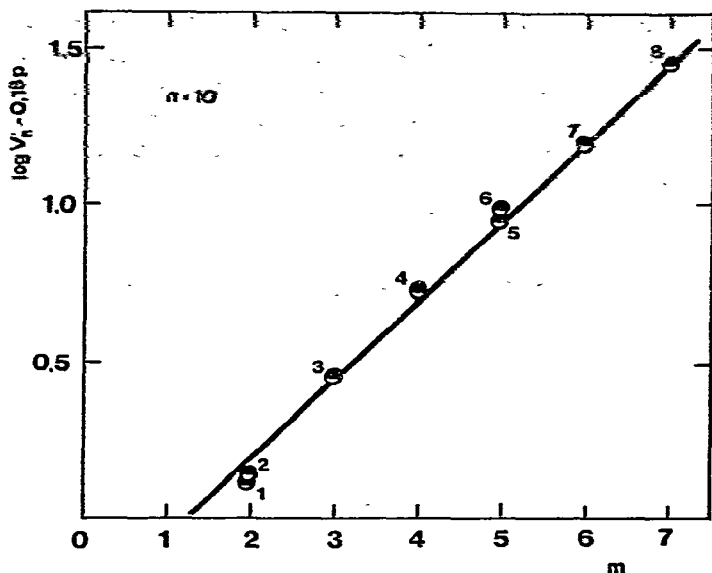


Fig. 2. Dependence of adjusted retention volumes (V'_R) on the number of double bonds (m) for individual functional groups (conjugated systems) at $n = 10$. Conditions as in Fig. 1. ●, Calculated values from Fig. 1 for: 1 = dienes; 2 = cyclodienes; 3 = alkylbenzenes; 4 = alkylvinylbenzenes; 5 = divinylbenzene; 6 = alkylnaphthalenes; 7 = diphenyl; 8 = phenanthrene and anthracene.

tion and the number of rings in the molecule of solute i , respectively, and $\Delta G^E(C)$, $\Delta G^E(X)$ and $\Delta G^E(Y)$ are the unit energy increments of the carbon atom, the double bond and the ring of the solute, respectively. The linearity of eqn. 1, and thus the linear dependence of $\log V'_R$ on the individual quantities n , m and p , are shown in Fig. 2, along with Fig. 1; Fig. 2 ($\log V'_R$ versus m) represents the dependence of $\log V'_R$ of a hypothetical series of compounds with ten carbon atoms on the number of conjugated double bonds (m). The $\log V'_R$ values for the individual z were read off from Fig. 1 at $n = 10$ and corrected by the average value of $\log V'_R$ for each ring in the molecule. An interesting behaviour was observed with the diphenyl group, the V'_R of which satisfies the above correlation expressions, although the molecule of this compound is regarded as imperfectly planar⁵⁵, and consequently its π -electron system is not conjugated.

Assuming the existence of only non-specific (disperse) interactions between the solute and the mobile phase, the individual terms in eqn. 1 can be interpreted so that $\Delta G^E(X)$ represents an interaction of the delocalized π -electron pair of the solute with the hydroxyl groups of the stationary phase, and $\Delta G^E(C)$ expresses the negative interaction of the carbon atom of the solute with the stationary phase (identical with a decrease in the mutual interaction of the polar groups of the stationary phase due to the presence of the carbon atom of the solute in this phase). The term $\Delta G^E(Y)$ can be expressed in two ways: either by an increase in polarity, or by a decrease in the effective size of the solute molecule owing to the cyclic structure formation. The latter hypothesis seems more acceptable, and the different gel chromatographic behaviour of cyclic and linear hydrocarbons⁵⁶, similarly to differences in the linear activity coefficients of cyclic and linear hydrocarbons in polar solvents^{51,57}, support its plausibility.

Table III gives the adjusted retention volumes of aromatic hydrocarbons, which in the sense of the above definition are polyfunctional derivatives, because all of their delocalized π -electrons are not conjugated. In the coordinates $\log V'_R$ versus n , binuclear aromatic compounds roughly satisfy the straight line of the diphenyl group, while trinuclear compounds correspond to the straight line of anthracene in Fig. 1. At the same time, Table III shows the accuracy of such approximations.

TABLE III

RETENTION DATA OF INCOMPLETELY CONJUGATED POLYPHENYLIC COMPOUNDS ON SPHERON P-300 IN *n*-HEPTANE

$\Delta \log V'_R = (\log V'_R - \log V'_R{}^{\text{th}}) / \log V'_R{}^{\text{th}}$ (see footnotes).

Compound	V'_R	n	z	$\Delta \log V'_R$
Dibenzyl	21.5	14	14	0.1212*
4,1-Diphenylethylene	16.9	14	16	0.0353*
2,2-Diphenylpropane	9.8	15	14	-0.0990*
Cyclohexylidenediphenylmethane	5.0	19	18	-0.0750*
6,6-Diphenylfulvene	13.2	18	22	-0.1225**
Triphenylmethane	14.9	19	22	-0.0152**
Benzyl- <i>p</i> -diphenyl	17.1	19	22	0.0353**
1,1,1-Triphenylethane	9.9	20	22	-0.0984**
Triphenylethylene	16.0	20	24	0.0874**
1,2,2-Triphenylpropane	11.5	21	22	0.0473**

* $V'_R{}^{\text{th}}$ is the theoretical value of V'_R of the alkyl derivative of diphenyl with the same n as the tested compound.

** $V'_R{}^{\text{th}}$ is the theoretical value of V'_R of the alkyl derivative of anthracene with the same n as the tested compound.

The results presented in this work do not provide proof of the LLC separation mechanism of the chromatographic system, because the length of the aliphatic chains of the tested compounds was not sufficient to justify an assumption of the linear decrease of retention in the case of long alkyl chains also⁴, typical of the LLC mechanism. On the other hand, it was shown that the separation mechanism of the above system exhibited characteristic features of LLC, such as a constant effect upon retention produced by each alkyl carbon atom and by each delocalized π -electron pair of the solute, as well as a considerable insensitivity of retention with respect to the other structural changes in the molecule of the solute. It would be difficult to interpret these properties by the LSC mechanism, in which, with the above system, one would expect a considerably smaller and less regular effect of the alkyl substitution on the retention of the compounds tested⁵⁸.

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