Journal of Chromatography, 95 (1974) 103–112

CHROM. 7490

GEL CHROMATOGRAPHIC BEHAVIOUR OF MONONUCLEAR AROMATIC HYDROCARBONS AND PHENOLS*

JIŘÍ ČOUPEK, SVATOPLUK POKORNÝ and JAN POSPÍŠIL

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6 (Czechoslovakia)

(Received March 29th, 1974)

SUMMARY

The gel chromatographic behaviour of aromatic hydrocarbons and phenols during elution with tetrahydrofuran in columns packed with styrene–divinylbenzene copolymer was investigated. From the elution volumes of 27 aromatic hydrocarbons and 80 phenols, conclusions were drawn about the effects of the types and positions of substituents and of the numbers and positions of phenolic hydroxyl groups on the elution volumes of these compounds in the system under investigation. The effects of the size of the alkyl substituents and of their positions with respect to the hydroxyl group of phenols were demonstrated, and the partial contributions of the alkyl and hydroxyl groups to the elution volumes were calculated. Chromatographic results were used for the characterization of the solvatability of phenolic molecules with tetrahydrofuran and as the basis of a discussion of problems of the steric hindrance of hydroxyl groups due to neighbouring substituents.

INTRODUCTION

The determination of the character and content of antioxidants in organic substrates is of concern in establishing their applicability under different technical conditions. The knowledge of these data is particularly important for polymeric products, especially with respect to their resistance to atmospheric ageing and oxidative degradation and to toxicological problems. In earlier papers[1–6], gel permeation chromatography was used, together with paper and thin-layer chromatography, for the analysis of phenolic antioxidants, investigation of changes in their concentration during the stabilization process and determination of some structural factors. These investigations revealed the existence of structural factors that affect the gel chromatography of phenols in tetrahydrofuran. Solvatability of the hydroxyl group, discussed by Yoshikawa *et al.*[7], was also considered among these factors.

* Presented at the 11th IUPAC Microsymposium on Macromolecules, Mechanisms of Inhibition Processes in Polymers, Prague, September 4–7, 1972; Paper E2.

In order to elucidate the overall influence of alkyl groups (their presence in the molecules of phenols is important from the viewpoint of antioxidative properties) on the chromatographic behaviour of solvatable and non-solvatable mononuclear aromatic compounds, series of alkylated aromatic hydrocarbons, isomeric mono-, di- and trialkylphenols, and mono- and dialkylhydroquinones and pyrocatechols, using styrene–divinylbenzene copolymer as the gel chromatographic packing of the columns and tetrahydrofuran as the eluent, were investigated in this work.

EXPERIMENTAL

Chemicals

Pure mono- and dihydric phenols and aromatic hydrocarbons obtained according to published methods or repurified commercial samples were used.

Gel chromatography

The elution volumes were determined on a gel chromatograph (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague) using five 1.2 m × 8 mm columns packed with S-gel-832 styrene–divinylbenzene copolymer (Institute of Macromolecular Chemistry, Czechosloavk Academy of Sciences, Prague). Tetrahydrofuran was used as the eluent after removal of the inhibitor, drying it over solid potassium hydroxide and distilling it on a packed column of 20 theoretical plates. A Waters Model R-403 differential flow refractometer was used as the detector. The compounds were injected as 1.5% solutions in tetrahydrofuran in volumes of *ca.* 0.2 ml and characterized by the elution volumes V_e in vol.c. (1 vol.c. (volume count) = 2.7 ml) and by the relative zone velocity V_0/V_e (V_0 = void volume = 47.0 vol.c.) while maintaining an elution rate of 30 ml/h. In order to discuss the effect of the alkyl and hydroxyl groups of the aromatic ring on the chromatographic behaviour of the compounds, we calculated the values $\Delta V_{e(OH)}$, $\Delta V_{e(OH)_2}$ and $\Delta V_{e(R)}$ as the difference between the elution volumes of reference aromatic hydrocarbons or phenols on the one hand, and the elution volume of the compound under investigation differing from the former by the presence of an OH group, several OH groups or an R group, on the other.

RESULTS AND DISCUSSION

The linear dimensions of the compounds analyzed, their volumes and their molecular weights must be considered in the separation of compounds by gel chromatography. Specifically, interactions with the solvent and the gel are of importance during transport through the column. These factors affect the elution volumes particularly in the case of solvatable aromatic compounds. From the results of investigations of the gel chromatographic behaviour of series of alkylated mononuclear phenols, the elution volumes of which, measured under the experimental conditions used, are summarized in Tables I–IV, some general conclusions were derived concerning the influence of the alkyl groups in the aromatic ring. Fundamental data on alkyl and hydroxyl groups were obtained by examining the behaviour of non-solvatable alkylbenzenes.

TABLE I

GEL CHROMATOGRAPHIC BEHAVIOUR OF AROMATIC HYDROCARBONS AND CYCLOHEXANE

V_e = elution volume in vol. c.; V_0/V_e = relative zone velocity; V_0 = 47.0 vol. c.; 1 vol. c. = 2.7 ml.

Compound	V_e	V_0/V_e	*Compound*	V_e	V_0/V_e
Cyclohexane	92.3	0.509	*p*-Xylene	90.0	0.522
Benzene	93.6	0.502	*p*-Cymene	84.9	0.554
Toluene	91.0	0.516	*p*-*tert.*-Butyltoluene	82.7	0.568
Ethylbenzene	89.8	0.523	Pseudocumene	89.2	0.527
4-Propylbenzene	86.3	0.545	Mesitylene	88.8	0.529
Isopropylbenzene	87.1	0.540	Pentamethylbenzene	89.2	0.527
tert.-Butylbenzene	85.0	0.553	Hexamethylbenzene	89.0	0.528
n-Amylbenzene	82.4	0.570	Hexaethylbenzene	77.4	0.607
n-Heptylbenzene	79.0	0.595	Naphthalene	91.5	0.514
n-Decylbenzene	74.4	0.632	α-Methylnaphthalene	90.0	0.522
o-Xylene	90.0	0.522	Diphenyl	87.9	0.535
m-Xylene	90.0	0.522	*m*-Terphenyl	82.6	0.569
3-Ethyltoluene	87.8	0.535	*p*-Terphenyl	82.6	0.569
m-Diisopropylbenzene	82.1	0.572			

Aromatic hydrocarbons

The elution volumes, V_e, of alkylbenzenes and of some polynuclear aromatic hydrocarbons are given in Table I. In the series of monoalkylbenzenes (C_1–C_{10} alkyl groups), for which the difference in the elution volume compared with that of benzene

TABLE II

GEL CHROMATOGRAPHIC BEHAVIOUR OF MONOHYDRIC ALKYL PHENOLS

Symbols as in Table I.

Compound	V_e	V_0/V_e	*Compound*	V_e	V_0/V_e
Phenol	83.0	0.566	2-*tert.*-Butyl-4-methylphenol	75.9	0.619
2-Methylphenol	82.8	0.568	2-*tert.*-Octyl-4-methylphenol	71.9	0.654
2-Ethylphenol	80.7	0.582	2,4-Di-*tert.*-butylphenol	70.8	0.664
2-Isopropylphenol	78.6	0.598	2-*tert.*-Octyl-4-*tert.*-butylphenol	68.2	0.689
2-*tert.*-Butylphenol	76.6	0.613	2,4-Di-*tert.*-octylphenol	65.5	0.718
2-*tert.*-Octylphenol	73.0	0.644	2,5-Dimethylphenol	81.3	0.578
2-Phenylphenol	79.5	0.591	2-*tert.*-Butyl-5-methylphenol	75.5	0.623
3-Methylphenol	81.8	0.575	2,6-Dimethylphenol	81.7	0.575
3-*tert.*-Butylphenol	76.8	0.612	2-Methyl-6-*tert.*-butylphenol	77.5	0.606
4-Methylphenol	81.7	0.575	2-Methyl-6-*tert.*-octylphenol	73.1	0.643
4-Ethylphenol	80.0	0.588	2,6-Di-*tert.*-butylphenol	75.0	0.627
4-Isopropylphenol	77.4	0.607	2,6-Di-*tert.*-octylphenol	67.9	0.692
4-*sec.*-Butylphenol	76.5	0.614	2,4,6-Trimethylphenol	80.8	0.582
4-*tert.*-Butylphenol	76.2	0.617	2,4-Dimethyl-6-*tert.*-butylphenol	76.1	0.618
4-*tert.*-Amylphenol	75.2	0.625	2,6-Dimethyl-4-*tert.*-butylphenol	75.1	0.626
4-*tert.*-Octylphenol	72.0	0.653	2,6-Dimethyl-4-*tert.*-octylphenol	70.9	0.663
4-Cyclohexylphenol	77.1	0.610	2-Methyl-4,6-di-*tert.*-butylphenol	71.7	0.656
4-Phenylphenol	78.2	0.601	2,6-Di-*tert.*-butyl-4-methylphenol	73.6	0.639
2,3-Dimethylphenol	81.5	0.577	2,4,6-Tri-*tert.*-butylphenol	70.0	0.671
2,4-Dimethylphenol	81.1	0.580	1-Naphthol	81.5	0.577
2-Methyl-4-*tert.*-butylphenol	77.0	0.610	2-Naphthol	81.0	0.580
2-Methyl-4-*tert.*-octylphenol	71.3	0.659			

TABLE III

GEL CHROMATOGRAPHIC BEHAVIOUR OF ALKYLPYROCATECHOLS

Symbols as in Table I.

Compound	V_e	V_0/V_e	*Compound*	V_e	V_0/V_e
Pyrocatechol	78.0	0.603	4-*tert.*-Amylpyrocatechol	71.9	0.654
2-Methylpyrocatechol	77.3	0.608	4-*tert.*-Octylpyrocatechol	69.1	0.680
3-Ethylpyrocatechol	75.8	0.620	4-*tert.*-Dodecylpyrocatechol	66.1	0.711
3-Isopropylpyrocatechol	74.5	0.631	3,5-Dimethylpyrocatechol	76.2	0.617
3-*sec.*-Butylpyrocatechol	73.8	0.637	3-Methyl-5-*tert.*-butylpyrocatechol	72.2	0.651
3-*tert.*-Butylpyrocatechol	73.2	0.642	3-Methyl-5-*tert.*-octylpyrocatechol	68.8	0.683
3-*tert.*-Octylpyrocatechol	69.5	0.676	3-*tert.*-Butyl-5-methylpyrocatechol	72.3	0.650
4-Methylpyrocatechol	77.2	0.609	3,5-Di-*tert.*-butylpyrocatechol	69.2	0.679
4-Ethylpyrocatechol	75.3	0.624	3,5-Di-*tert.*-octylpyrocatechol	64.2	0.732
4-Isopropylpyrocatechol	74.3	0.633	3,6-Dimethylpyrocatechol	77.6	0.606
4-*n*-Butylpyrocatechol	72.3	0.650	3-Methyl-6-*tert.*-butylpyrocatechol	73.0	0.644
4-*sec.*-Butylpyrocatechol	72.3	0.650	3,6-Di-*tert.*-butylpyrocatechol	70.3	0.669
4-*tert.*-Butylpyrocatechol	72.3	0.650			

is affected by a single aliphatic substituent. $\Delta V_{e(R)}$ varies in the range 2.6–19.2 vol.e. (Table VII). In the derivatives substituted with a normal alkyl group, $\Delta V_{e(R)}$ increases with the number of carbon atoms in the chain. A branched alkyl group has a smaller effect on the elution volume of alkylbenzenes than a normal alkyl group with the same number of carbon atoms (indicated by a comparison between propylbenzene and isopropylbenzene). In accordance with the results obtained for alkylphenols, the influence of the alkyl group on the elution volume is usually reduced if the volume of the basic molecular skeleton increases. This can be seen if the effects of the methyl group in the benzene and naphthalene series are compared: $\Delta V_{e(Me)}$ calculated from the elution volume of toluene is 2.6 while that calculated from α-methylnaphthalene is 1.5 (Table I).

Further results were obtained from an investigation of the elution volumes of higher alkylbenzenes. In the series of 1,4-dialkyl derivatives, the elution volume remains unaffected by the mutual interaction of both substituents. With the exception of a low value of $\Delta V_{e(Me)}$ calculated for substitution with two methyl groups (*p*-xylene), the other values of $\Delta V_{e(R)}$, including $\Delta V_{e(Me)}$ calculated from various 1,4-di-

TABLE IV

GEL CHROMATOGRAPHIC BEHAVIOUR OF ALKYLHYDROQUINONES, RESORCINOL AND PYROGALLOL

Symbols as in Table I.

Compound	V_e	V_0/V_e	*Compound*	V_e	V_0/V_e
Hydroquinone	77.2	0.609	2,5-Di-*tert.*-butylhydroquinone	67.8	0.693
2-Methylhydroquinone	76.4	0.615	2,6-Dimethylhydroquinone	75.5	0.623
2-Isopropylhydroquinone	73.4	0.640	2-Methyl-6-*tert.*-butylhydroquinone	72.1	0.652
2-*tert.*-Butylhydroquinone	72.1	0.652	2,6-Di-*tert.*-butylhydroquinone	69.7	0.674
2,5-Dimethylhydroquinone	75.7	0.621	Resorcinol	77.0	0.610
2-Methyl-5-*tert.*-butylhydroquinone	71.2	0.660	Pyrogallol	74.3	0.633

alkylbenzenes containing a methyl group combined with another alkyl group or two other alkyl groups, coincide with those obtained from the elution volumes of monoalkylbenzenes. The additivity of the contributions of the individual substituents in the total change in the elution volume of benzene is valid in this instance.

The conclusion concerning $\Delta V_{e(R)}$ values calculated for the series of 1,4-dialkylbenzenes also holds for 1,3-dialkylbenzenes; $\Delta V_{e(R)}$ values calculated for this series are given separately in Table VII. Although in this series of isomeric dialkylbenzenes there is no important mutual steric influence between the substituents under investigation, the elution volume of derivatives that contain two bulky substituents is reduced less than would correspond to the additivity of the individual substituents. This can be seen by comparing the $\Delta V_{e(i\text{-}Pr)_2}$ values calculated for cumene and *m*-diisopropylbenzene.

Of the 1,2-dialkylbenzenes, only *o*-xylene was chromatographed: $\Delta V_{e(2Me)}$ is the same as for the other isomeric xylenes. The decrease in the elution volume of all three isomeric xylenes compared with benzene is characterized by $\Delta V_{e(3Me)} = 3.6$ vol.c. The value of $\Delta V_{e(3Me)}$ for isomeric trimethylbenzenes, pentamethylbenzene and hexamethylbenzene lies within the range 4.4–4.8 vol.c. In the whole series of methylbenzenes under investigation, the largest change in the elution volume compared with benzene was caused by the first methyl group, and the effect of the introduction of further methyl groups gradually became less pronounced. Hence, owing to the steric arrangement of the molecules of polymethylbenzenes, the individual compounds cannot be distinguished, even on highly effective gel chromatographic columns.

From the elution volumes of diphenyl and the isomeric terphenyls, a value of $\Delta V_{e(phenyl)} = 5.3$–$5.7$ vol.c. was calculated. For terphenyls, this value is independent of the mutual positions of the aryl groups. The elution volume of naphthalene (two condensed aromatic rings) is reduced by 2.1 vol.c. compared with benzene, that is, by a value which lies within the range of the $\Delta V_{e(Me)}$ values valid for the benzene and naphthalene series.

The loss of aromaticity of the benzene ring as a result of hydrogenation is reflected in gel chromatography in accordance with changes in the steric requirement of the six-membered ring in a decrease in the elution volume. Compared with benzene, the V_e value of cyclohexane is reduced by 1.3 vol.c. Such a difference in the elution volumes of these two unsubstituted six-membered rings is comparatively small. As a consequence, no clear difference between the $\Delta V_{e(R)}$ values of radicals derived from these molecules and bonded to the benzene ring can be expected. For the sake of comparison, a value of $\Delta V_{e(cyclohexyl)} = 5.9$ vol.c. (calculated from the elution volume of 4-cyclohexylphenol) can be given together with the already mentioned values of $\Delta V_{e(phenyl)}$.

Mononuclear phenols

The investigation of the behaviour of mononuclear phenols in gel chromatography was carried out with a series of mononuclear mono-, di- and trialkylphenols and dihydric mono- and dialkylphenols. The elution volumes are given in Table II; they enabled us to calculate the changes in the elution volumes, $\Delta V_{e(OH)}$, due to the presence of a solvatable hydroxyl group compared with similarly alkylated benzenes and monohydric phenols, the overall effect of the hydroxyl groups in dihydric phenols $\Delta V_{e(2OH)}$, and also changes in the elution volumes of phenols, $\Delta V_{e(R)}$, that arise because

of the presence of the alkyl groups (from a comparison with non-alkylated or less alkylated phenols).

The steric effect of alkyl groups in positions *ortho* to the hydroxyl group decreases the solvatability of phenol[1,7,8]; the molar volume of phenol, according to Edwards and Ng[9], increases by 55–65 ml/mole owing to the solvation of tetrahydrofuran. The above data were obtained from the results of chromatography of some monohydric phenols. Under the conditions examined, it was found that the largest change in the elution volume of non-alkylated benzene is caused by the introduction of the first hydroxyl group (Table V); the second hydroxyl group contributes considerably less (the V_e value of dihydric phenols differs from that of phenol by 5.0–6.0 vol.c., in contrast with $\Delta V_{e_{OH}}$ = 10.6 vol.c. for phenol). Owing to the partly reduced solvatability due to the presence of intramolecular hydrogen bonds, the elution volume of pyrocatechol is higher than that of its isomers hydroquinone and resorcinol. In accordance with these results, it was found that the presence of three *vicinal* hydroxyl groups reduces the elution volume by an amount that is less than that which corresponds to the sum of the contributions of the individual hydroxyl groups (compared with resorcinol and pyrocatechol, V_e is changed by 2.7 or 3.7 vol.c.). This reduced solvatability gives, as a consequence, a lower $\Delta V_{e_{OH}}$ of 1-naphthol (10.0 vol.c.) compared with 2-naphthol (10.5 vol.c.).

TABLE V

VALUES OF $\Delta V_{e_{OH}}$ IN VOL. C. FOR MONONUCLEAR MONOHYDRIC PHENOLS

Compound	$\Delta V_{e_{OH}}$	*Compound*	$\Delta V_{e_{OH}}$
Phenol	10.6	2,4-Dialkylphenol	8.9
2-Alkylphenol	8.2–9.1	2,5-Dialkylphenol	8.7
3-Alkylphenol	8.2–9.2	2,6-Dialkylphenol	8.3
4-Alkylphenol	8.8–9.8	2,4,6-Trialkylphenol	8.0
2,3-Dialkylphenol	8.7		

The change in the elution volume, $\Delta V_{e_{OH}}$, in the series of three isomeric monoalkylphenols caused by the presence of the hydroxyl group, in contrast with alkylbenzene, is largest for 4-alkylphenols, in which the hydroxyl group remains sterically unaffected by the alkyl group. The $\Delta V_{e_{OH}}$ values for 3-alkyl- and 2-alkylphenols are identical and lower than those for the 4-isomers. For all three isomeric series, the $\Delta V_{e_{OH}}$ values lie within a range of 1 vol.c. However, not even for 2-alkylphenols is $\Delta V_{e_{OH}}$ influenced by the volume of the C_1–C_4 alkyl group present, compared with similarly substituted alkylbenzenes; the same holds for $\Delta V_{e_{OH}}$ values calculated for 2-phenylphenol. This result indicates that a single alkyl group in a position *ortho* to the hydroxyl group has a low steric effect on the solvatability of the hydroxyl group. A similar conclusion also follows from the results of the investigation of isomeric dialkylphenols that have one substituent in an *ortho* position (2,3-dialkyl-, 2,4-dialkyl- and 2,5-dialkylphenols), or with both *ortho* positions to the hydroxyl group alkylated (2,6-dialkylphenols). The same holds to a great extent for 2,4,6-trialkylphenols. However, the conclusion drawn for higher alkylphenols holds only for methyl derivatives, *i.e.*, sterically unhindered (there being no corresponding di- or trialkylbenzenes avail-

able for the calculation of the $\Delta V_{e(OH)}$ values of cryptophenols or sterically hindered phenols). The examination of the series of monohydric phenols showed that the elution volume of unsubstituted benzene or naphthalene is altered by 10.0–10.6 vol.e. if a single hydroxyl group is introduced. The elution volume of sterically unhindered phenols compared with similarly alkylbenzenes is reduced by 8.0–9.8 vol.e.

By choosing suitably comparable compounds in the pyrocatechol series, it is possible to investigate the effect of the presence of hydroxyl groups in position 1 or 2 (comparison with the elution volumes of alkylphenols) and the overall effect of both hydroxyl groups (comparison with alkylbenzenes). The $\Delta V_{e(1\text{-}OH)}$, $\Delta V_{e(2\text{-}OH)}$ and $\Delta V_{e(2OH)}$ values are listed in Table VI. From the results obtained for 3-alkylpyrocatechols, it is evident that, probably owing to the presence of two hydroxyl groups, the effect on the $\Delta V_{e(OH)}$ values of the alkyl group in the position *ortho* to the hydroxyl group is more pronounced than that for 2-alkylphenols. Both the $\Delta V_{e(1\text{-}OH)}$ and $\Delta V_{e(2\text{-}OH)}$ values are reduced as the molecular volume of the alkyl group increases. For 4-alkylpyrocatechols, $\Delta V_{e(1\text{-}OH)}$ is virtually independent of the volume of the alkyl group (comparison with the elution volumes of 3-alkylphenols); $\Delta V_{e(2\text{-}OH)}$ is lower for compounds that contain bulky alkyl groups (comparison with 4-alkylphenols). The results calculated for both isomeric series of dialkylpyrocatechols, especially for the compounds with a bulky alkyl group in position 3, are in accordance with the described trends of the influence of the volume of the alkyl group on $\Delta V_{e(OH)}$. In general, the differences between the elution volumes of alkylpyrocatechols compared with the elution volumes of monohydric alkylphenols caused by the presence of a second hydroxyl group are less than the $\Delta V_{e(OH)}$ values calculated from the elution volumes of monohydric alkylphenols. The total contribution of both hydroxyl groups, *i.e.*, $\Delta V_{e(2OH)}$, in alkylpyrocatechols compared with alkylbenzenes is smaller than the corresponding value for a non-alkylated pyrocatechol. With respect to the overall steric requirements of molecules, the change in the volume of the molecule caused by a further substituent is less pronounced for bulkier molecules.

TABLE VI

VALUES OF $\Delta V_{e(OH)}$ AND $\Delta V_{e(2OH)}$ IN VOL. C. FOR MONONUCLEAR DIHYDRIC PHENOLS

Compound	$\Delta V_{e(1\text{-}OH)}$	$\Delta V_{e(2\text{-}OH)}$	$\Delta V_{e(4\text{-}OH)}$	$\Delta V_{e(2OH)}$
Pyrocatechol		5.0		15.6
3-Alkylpyrocatechol	3.4–5.5	3.6–4.5		11.8–13.7
4-Alkylpyrocatechol	4.5–4.6	2.9–4.7		12.7–14.5
3,5-Dialkylpyrocatechol		1.3–4.9		13.8
3,6-Dialkylpyrocatechol		2.5–3.7		12.4
Resorcinol				16.6
Hydroquinone			5.8	
2-Alkylhydroquinone	4.7–5.4		4.5–6.4	12.9–14.6
2,5-Dialkylhydroquinone			4.3–5.6	14.3
2,6-Dialkylhydroquinone			5.3–6.2	14.5

Compounds of the hydroquinone series have two symmetrically situated and mutually unaffected groups that can be solvated by the eluent. Alkylation of the ring has no important effect on $\Delta V_{e(2OH)}$. By using suitable isomeric monohydric phenols, we calculated the $\Delta V_{e(OH)}$ values for hydroxyl groups with both *ortho* positions free

TABLE VII

VALUES OF $\Delta V_{e(R)}$ IN VOL. C. FOR THE INDIVIDUAL SUBSTITUENTS R IN ALKYLBENZENES AND PHENOLS

R	$\Delta V_{e(R)}$		$\Delta V_{e(para\text{-}R)}$				$\Delta V_{e(meta\text{-}R)}$	
	Monoalkyl- and 1,4-dialkylbenzenes	1,3-Dialkylbenzenes	4-Alkylphenols	2,4-Dialkylphenols	2,4,6-Trialkylphenols	4-Alkylpyrocatechols	3,5-Dialkylpyrocatechols	2,5-Dialkyl- and 3-alkylphenols
Methyl	2.0–2.6*	2.0*	1.3	0.7–1.7	0.9–1.4	0.8	0.9	1.1–1.5
Ethyl	3.8	3.2	3.0			2.7		
n-Propyl	7.3							
Isopropyl	6.1–6.5	5.0	5.6			3.7		
sec.-Butyl			6.5			5.7		
tert.-Butyl	8.3–8.6		6.8	4.8–5.8	5.0–5.8	5.7	4.0–4.9	6.2
n-Amyl	11.2							
tert.-Amyl			7.8			6.1		
Cyclohexyl			5.9					
n-Heptyl	14.6							
tert.-Octyl[a]			11.0	7.5–10.5	10.8	8.9	5.3–8.5	
n-Decyl	19.2							
tert.-Dodecyl[b]						11.9		
Phenyl	5.3–5.7	5.3	4.8					

* For *p*-xylene or *m*-xylene 1.0.
** Low values, if the other *ortho* substituent is bulky.
*** Low values for cryptophenols or sterically hindered phenols.
[a] 1,1,3,3-Tetramethylbutyl.
[b] 1,1,3,3,5,5-Hexamethylhexyl.

(from the elution volumes of hydroquinone and 2-alkyl- and 2,6-dialkylhydroquinones), for hydroxyl groups substituted in one *ortho* position (from 2-alkyl- and 2,5-dialkylhydroquinones) and in both *ortho* positions (from 2,6-dialkylhydroquinones).

All of the $\Delta V_{e(OH)}$ values thus calculated lie within a narrow range from 4.3 to 6.4 vol.c. The presence of two solvatable hydroxyl groups reduces the elution volume compared with similarly alkylated benzenes in all mono- and dialkylhydroquinones.

The contributions of the alkyl groups, $\Delta V_{e(R)}$, were determined from the differences between the elution volumes of mono- and dihydric phenols and those of their alkyl derivatives. The values of $\Delta V_{e(para\text{-}R)}$ and $\Delta V_{e(meta\text{-}R)}$ are characteristic of alkyl groups unaffected by the substitution in adjacent *ortho* positions (Table VII). They were calculated from five series of mono- and dialkylphenols. As to the effect of the character of the alkyl group, the decrease in V_e corresponds to the presence of the alkyl groups with increasing volume. The $\Delta V_{e(para\text{-}R)}$ values are lower than the $\Delta V_{e(R)}$ values of the same alkyl groups (or of the phenyl group) calculated for alkylbenzenes. For a bulkier base for which the changes in the elution volumes caused by the alkyl group have been calculated, the $\Delta V_{e(R)}$ values are lower. These values decrease in the indi-

$\Delta V_{e(ortho-R)}$	2-Alkylphenols	2,4-Dialkylphenols	2,6-Dialkylphenols	2,5-Dialkylphenols	2,3-Dialkylphenols	2,4,6-Trialkylphenols	3-Alkylpyrocatechol	3,5-Dialkylpyro-catechol	3,6-Dialkylpyro-catechol	2-Alkylhydroquinone	2,5-Dialkylhydro-quinone	2,6-Dialkylhydro-quinone
0.2		−0.8–0.7	0.9–1.1	0.5	0.5	0.9–1.9	0.7	0.1–1.0	0.3–0.2	0.8	0.7–0.9	0.0–0.9
2.3							2.2					
4.4							3.5			3.8		
6.4		5.4–5.8	1.6**–5.3	6.3		0.8***–5.3	4.8	3.1–4.9	2.9–4.3	5.1	4.3–5.2	2.4–4.3
10.0		6.5**–9.8					8.5	4.9				
3.5												

vidual series in the order alkylbenzenes → alkylphenols → alkylpyrocatechols. The change in the elution volume of both phenolic types due to a certain substituent is always less pronounced for higher alkylated compounds, particularly if there are bulky alkyl groups present at the same time in positions *ortho* to the hydroxyl group. As an example, one may quote the values of $\Delta V_{e(para-R)}$ for the 1,1,3,3-tetramethylbutyl (*i.e.*, *tert.*-octyl) group, which vary for monoalkylphenols from 8.9 to 11.0 vol.e., for dialkylphenols with combined methyl and *tert.*-octyl groups from 8.5 to 10.5 vol.e., and for analogues combined with another tertiary alkyl group from 5.3 to 7.5 vol.e. If, on the other hand, in 2,4,6-trialkylphenols, for example, both *ortho*-alkyl groups are small, then the change in the elution volume due to the *para*-alkyl group is commensurate with the change calculated from the values of an identically alkylated 4-alkylphenol. For most individual R groups investigated, the $\Delta V_{e(para-R)}$ values vary in the phenol series considered here only within a very narrow range, and are therefore well suited for the purposes of characterization.

From twelve different groups of alkylphenols, pyrocatechols and hydroquinones, the $\Delta V_{e(ortho-R)}$ values (Table VII) were calculated. From the total steric re-

quirements of the molecules of phenols, it follows that a change in the elution volume due to the alkyl group in the position *ortho* to the solvated hydroxyl group will be less pronounced than a change due to the presence of the same alkyl group in the *meta* or *para* position. The factors mentioned above also apply in this instance: firstly the volume of the basic skeleton of the type of compounds under investigation and, consequently, the number and character of further substituents present in the compound. This can be seen for all of the types of compounds examined in this work. For instance, the presence of a methyl group in the position *ortho* to the hydroxyl group need not be reflected in a change in the elution volume (or may be reflected in a change only within the limits of experimental error), if the phenol molecule contains another bulky substituent in the *para* position and especially in the second *ortho* position. The same holds for the bulky *tert.*-butyl groups in cryptophenols, and predominantly in sterically hindered phenols. The alkyl groups in 3,6-dialkylpyrocatechols and 2,6-dialkylhydroquinones affect the elution volumes less than the alkyl groups in the *ortho* positions in other derivatives of pyrocatechol and hydroquinone.

The additivity of the effect of the alkyl groups in polyalkyl derivatives was investigated by means of the elution volumes determined experimentally and of the $\Delta V_{e,R}$ values calculated from the individual isomeric monoalkylphenols, pyrocatechols and 2-alkylhydroquinones, which could be estimated for those series in which several compounds were investigated (Table VII). The difference between the calculated and experimentally determined values of $\Delta V_{e,\Sigma R}$ is very small in the series of monohydric phenols for 2,4-, 2,5- and 2,6-dialkylphenols and 2,4,6-trialkylphenols, in all instances with the exception of derivatives substituted in both *ortho* positions or each time in one *ortho* and one *para* position with two bulky alkyl groups, and of derivatives containing three bulky alkyl groups. In such instances, the $\Delta V_{e,\Sigma R}$ values determined experimentally are always lower than the calculated values. The same conclusion is valid for the derivatives of the pyrocatechol and hydroquinone series investigated in this work.

REFERENCES

1 J. Čoupek, J. Kahovec, M. Křiváková and J. Pospíšil, *Angew. Makromol. Chem.*, 15 (1971) 137.
2 J. Čoupek, S. Pokorný, L. Jiráčková and J. Pospíšil, *J. Chromatogr.*, 75 (1973) 87.
3 L. Zikmund, L. Taimr, J. Čoupek and J. Pospíšil, *Eur. Polym. J.*, 8 (1972) 83.
4 J. Protivová, J. Pospíšil and L. Zikmund, *J. Polym. Sci., Part C*, 40 (1973) 233.
5 J. Čoupek, S. Pokorný, J. Protivová, J. Holčík, M. Karvaš and J. Pospíšil, *J. Chromatogr.*, 65 (1972) 279.
6 S. Pokorný, J. Čoupek and J. Pokorný, *J. Chromatogr.*, 71 (1972) 576.
7 T. Yoshikawa, K. Kimura and S. Fujimura, *J. Appl. Polym. Sci.*, 15 (1971) 2513.
8 J. G. Hendrickson, *Anal. Chem.*, 40 (1968) 49.
9 G. D. Edwards and Q. Y. Ng, *J. Polym. Sci., Part C*, 21 (1968) 105.