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ANTIOXIDANTS AND STABILIZERS

XLVII*. BEHAVIOUR OF AMINE ANTIOXIDANTS AND ANTIOZONANTS AND MODEL COMPOUNDS IN GEL PERMEATION CHROMATOGRAPHY**

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SUMMARY

The behaviour of some amine antioxidants and antiozonants and of some model substances (phenols, aromatic hydrocarbons, and amines) during gel permeation chromatography are reported. The investigation was carried out on a polystyrene gel chromatograph with tetrahydrofuran as the solvent, at 30°. The elution volumes were found and the molar volumes determined by calibration with standard hydrocarbons. The behaviour of the amine compounds is characterized with respect to the important structural factors affecting their elution volumes. The gel permeation chromatographic analysis of amine stabilizers in polyolefins and rubbers can be combined with other methods for qualitative and quantitative determination.

INTRODUCTION

The identification and determination of stabilizers in polymers are very difficult, especially in rubbers and their vulcanizates. These compounds are added to the polymers in very low concentrations, and their determination sometimes is rendered still more difficult by further additives (*e.g.*, plasticizers, fillers, dyes, vulcanization accelerators, retarders, and products of their oxidation or thermic transformation, etc.), which are present in greater concentrations.

The aromatic amines rank among the most active oxidation inhibitors, breaking kinetic autoxidation chains or preventing ozonolysis. However, their disadvantage consists in a transformation into coloured oxidation products which impart an intensive colour to the products. This is why they are primarily used for the stabilization of polymers in which this does not matter: mainly for rubber and, to a limited extent, polyethylene, polypropylene, polystyrene, and polyamides[1,2]. On an industrial scale, polynuclear aromatic amines, diaryl amines, arylene diamines, their derivatives, and the condensation products of amines are predominantly used.

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A number of authors have attempted to analyze the amine antioxidants and antiozonants because of their technical importance. Chromatographic methods were used for qualitative determinations in most cases. Thin-layer chromatography on silica gel layers with various solvent systems has been the method most frequently used[3–20]. Antioxidants contained in rubber extracts were analyzed by paper[15,21–23] or gas–liquid chromatography[24–27]. Quantitative determinations are best carried out by physical methods, such as spectrophotometry[14,16,21,28,29], nuclear magnetic resonance and mass spectrometry[29]. The stabilizers are first extracted from the polymer by an appropriate organic solvent. Determination directly in the polymers is possible by the luminescence method[28]. The most recent findings in the field of analysis of amine antioxidants and antiozonants were summarized by Crompton[20].

The gel permeation chromatographic (GPC) method, which has proved useful for other types of stabilizers, has not yet been used in their determination[30–34]. So far, this method has been applied in the analysis of some rather simple aromatic amines, and their behaviour has been compared to that of similar hydrocarbons, alcohols and esters[35,36]. The work reported here is devoted to the GPC analysis of important amine antioxidants and antiozonants. The experimental results obtained with the individual stabilizers are used in analyses of rubber extracts and in the investigation of the loss or transformation of the active stabilizing component during oxidation and ageing of the polymers.

EXPERIMENTAL

Chemicals

Commercial samples of amine stabilizers and pure aromatic model compounds (hydrocarbons, amines, phenylene diamines and phenols) were used for the investigation of gel chromatographic behaviour. The trade names and producers of the stabilizers are listed in the notes to Table II. Standard aliphatic hydrocarbons and esters were used for calibration.

Gel chromatography

The samples were analyzed on a gel chromatograph built in the Institute of Macromolecular Chemistry. Tetrahydrofuran (THF), distilled prior to use, was used as the elution agent. The chromatographic system consisted of a series of six stainless-steel columns (1200×8 mm) and was connected to an R403 flow refractometer (Waters Ass., Framingham, Mass., U.S.A.) and to a 254 nm flow UV analyzer (Development Works of the Czechoslovak Academy of Sciences, Prague). The data provided by both detectors and the photocell which was used for checking the volume of the elution agent were recorded. The measurements were carried out at 30°, the flow-rates of the elution agent through the columns were 35–45 ml/h and the pressure in the columns was about 5 atm. The columns were packed with Copolymer ST-DVB, No. IX polystyrene gel (United Chemical and Metallurgical Works, Ústí, Czechoslovakia), 0.040–0.056 mesh. The samples were injected as 2–5% solutions in THF in amounts of about 0.5±0.1 ml into the columns. The elution volumes, V_e, characteristic of each compound in the given system and corresponding to the size of the molecules of the given compound in THF solution, were determined.

Since the GPC method does not allow a direct determination of the molecular

weights or molar volumes of the samples under investigation, calibration was made by using standard compounds in the form of a graphic dependence of their molar volume on the elution volume[35–40]. Normal hydrocarbons (pentane, hexane, heptane, dodecane, hexadecane, octadecane) and aliphatic esters (octyl adipate and octyl sebacate) were used as standards. The molar volumes (ml/mole) were plotted against elution volumes, V_e (ml), in the calibration curves, as shown in Table I. The molar volumes were calculated from the atomic volumes and structural coefficients[36].

TABLE I

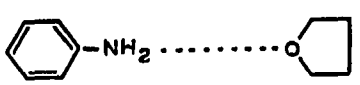
THE BEHAVIOUR OF STANDARD COMPOUNDS IN GPC AND MOLAR VOLUMES CALCULATED AFTER REF. 36

Compound	*Molecular weight*	*Molar volume (ml/mole)*	V_e *(ml)*
n-Pentane	72.15	118.4	246
n-Hexane	86.18	140.6	239
n-Heptane	100.20	162.8	233
n-Dodecane	170.33	273.8	220
n-Hexadecane	226.43	362.6	212
n-Octadecane	254.48	414.4	206
Octyl adipate	270.14	495.4	200
Octyl sebacate	326.24	613.8	192

RESULTS AND DISCUSSION

The results of the GPC measurements of the elution volumes of aromatic amines under investigation, their molecular weights, calculated molar volumes and the effective molar volumes observed and read from the calibration curves are given in Table II. A comparison of the calculated and effective molar volumes revealed deviations in the behaviour of all amines investigated here, compared to similar aliphatic hydrocarbons.

The behaviour of the compounds in THF solution and in contact with a swollen gel is affected by several factors. We deduce from literature data[35,37,38] and from experimental data obtained by measurements of various types of compounds that, similarly to phenols, the gel chromatographic behaviour of aromatic amines is predominantly affected by the formation of solvates due to intermolecular hydrogen bonds between the amine and ether groups of THF.



Solvation with tetrahydrofuran leads to an increase in the volume of the molecule of the aromatic amine under investigation and a decrease in V_e. To make possible a comparison with the behaviour of aromatic amines, data on selected alkyl phenols are given in Table III, measured under comparable conditions.

TABLE II

THE BEHAVIOUR OF AMINIC ANTIOXIDANTS, ANTIOZONANTS AND MODEL COMPOUNDS IN GPC

Trade names and producers are given in notes.

Chemical structure	*Molecular weight*	*V_e (ml)*	*Molar volume (ml/mole)*		*Deviation*
			Calculated	*Effective*	
Aniline	93.12	238	110.2	150.3	+ 40.1
4-Methylaniline	107.15	238	132.4	150.3	+ 17.9
2,3-Dimethylaniline	121.18	247	154.6	115.6	− 39.0
2,4,6-Trimethylaniline	135.20	232	168.8	183.2	+ 14.4
2,3,5,6-Tetramethylaniline	149.24	247	199.0	115.6	− 83.4
N-Methylaniline	107.15	253	133.9	95.9	− 38.0
N,N-Dimethylaniline	121.18	278	156.1	44.2	−111.9
1-Naphthylamine	143.18	242	161.8	134.9	− 26.9
2-Naphthylamine	143.18	241	161.8	139.0	− 22.8
Diphenylamine	169.22	229	200.3	201.0	+ 0.7
Phenyl-2-naphthylamine[a]	219.27	235	251.9	166.7	− 85.2
o-Phenylenediamine	108.14	238	124.4	150.3	+ 25.9
m-Phenylenediamine	108.14	220	124.4	266.1	+141.7
p-Phenylenediamine	108.14	248	121.4	111.4	− 10.0
4-Aminodiphenylamine	184.23	221	214.5	257.6	+ 43.1
4,4′-Bis-(dimethylamino)diphenylamine	255.41	228	320.5	212.3	−108.2
Benzidine	184.23	217	213.0	291.7	+ 78.7
o-Tolidine	212.28	224	257.4	234.4	− 23.0
N,N′-Dimethyl-*p*-phenylenediamine	136.22	247	171.8	115.6	− 56.2
N,N′-Diethyl-*p*-phenylenediamine	164.14	222	216.2	249.5	+ 33.3
N,N′-Di-*sec*-butyl-*p*-phenylenediamine[b]	220.38	236	305.0	162.2	−142.8
N,N′-Di-*iso*-heptyl-*p*-phenylenediamine[c]	304.54	202	438.2	462.4	+ 24.2
N,N′-Di-*iso*-octyl-*p*-phenylenediamine[d]	332.58	200	482.6	495.5	+ 12.9
N,N,N′-trimethyl-*p*-phenylenediamine	150.28	252	186.0	98.9	− 87.1
N,N′-Dimethyl-2-methyl-*p*-phenylenediamine	150.28	250	186.0	105.2	− 80.8
N,N′-Diphenyl-*p*-phenylenediamine[e]	260.36	208	304.6	384.5	+ 79.9
N,N′-Dinaphthyl-*p*-phenylenediamine[f]	360.46	205	415.2	421.7	+ 6.5
N-*iso*-Propyl-N′-phenyl-*p*-phenylenediamine[g]	226.34	222	282.6	249.5	− 33.1
N-*iso*-Butyl-N′-phenyl-*p*-phenylenediamine[h]	240.36	214	304.8	319.9	+ 15.1
N-Cyclohexyl-N′-phenyl-*p*-phenylenediamine[i]	266.41	206	326.8	410.2	+ 83.4
N-Octyl-N′-phenyl-*p*-phenylenediamine[k]	296.47	206	393.6	410.2	+ 16.6
N,N′-Bis-4-(N,N-dimethylamino)-phenyl-*p*-phenylenediamine	346.55	218	424.8	283.1	−141.7

[a] Age Rite Powder (Anchor Chemical Company Ltd., Manchester, Great Britain).
[b] Topanol M (I.C.I., Macclesfield, Great Britain).

[c] Santoflex 77 (Monsanto, St. Louis, Mo., U.S.A.).
[d] UOP 88, UOP 288 (UOP Chemical Company, East Rutherford, N.J., U.S.A.).
[e] DPPD (Monsanto), Altofane DIP (Etablissements Kuhimann, Paris, France), JZF (U.S. Rubber Co., Naugatuck Chemical Division, New York, N.Y., U.S.A.).
[f] Santowhite CI (Monsanto), Antioxidant 123 (Anchor), DNPD (Chemical Works of J. Dimitrov, Bratislava, Czechoslovakia), ASM DNP (Bayer, Leverkusen, G.F.R.).
[g] ASM 4010 NA (Bayer), Nonox ZA (Arnold, Hoffman & Co., Providence, R.I., U.S.A.).
[h] Santoflex 13 (Monsanto).
[i] Flexzone 6-H (U.S. Rubber Co., Naugatuck Division).
[k] UOP 688 (UOP).

TABLE III

THE BEHAVIOUR OF SELECTED AROMATIC HYDROCARBONS AND PHENOLS IN GPC

Chemical structure	*Molecular weight*	V_e *(ml)*	*Molar volume (ml/mole)*		*Deviation*
			Calculated	*Effective*	
Benzene	78.11	278.0	96.0	44.2	−51.8
Toluene	92.14	256.0	118.2	87.5	−30.7
m- and *p*-Xylenes	106.16	255.0	140.4	90.2	−30.2
Ethylbenzene	106.16	247.0	140.4	115.6	−24.8
Mesitylene	120.18	255.0	154.6	90.2	−64.4
Pseudocumene	120.18	254.0	154.6	92.7	−61.9
Cumene	120.18	241.0	162.6	139.0	−23.6
p-Cymene	134.21	245.0	184.8	122.5	−62.3
1,2,4,5-Tetramethylbenzene	134.21	252.0	184.8	98.9	−85.9
tert.-Butylbenzene	134.21	242.0	184.8	134.9	−49.9
Naphthalene	128.16	255.0	147.6	90.2	−57.4
Diphenyl	154.20	241.0	162.6	139.0	−23.6
Phenol	94.11	240.0	105.9	142.9	+37.0
o-, *m*- and *p*-Cresols	108.13	237.0	128.1	157.4	+28.7
2- and 4-Ethylphenols	122.16	235.0	100.3	166.7	+16.4
2-*n*-Propylphenol	136.19	229.0	164.5	201.0	+36.5
2,4-Dimethylphenol	122.16	233.0	150.3	177.9	+27.6
2,3-Dimethylphenol	122.16	238.0	150.3	150.3	0.0
2,6-Dimethylphenol	122.16	239.0	150.3	147.9	− 2.4
2,4,6-Trimethylphenol	136.19	237.0	164.5	157.4	− 7.1
2- and 4-Phenylphenols	170.20	233.0	194.5	177.9	−16.6
2-Naphthol	144.16	251.0	157.5	101.6	−55.9
o-Aminophenol	109.12	242.0	130.1	134.9	+ 4.8
m-Aminophenol	109.12	226.0	130.1	221.3	+91.2
p-Aminophenol	109.12	242.0	130.1	134.9	+ 4.8
Tetrahydrofuran	72.10	–	88.3	–	–

The increase in the elution volume is affected by changes in the pore size of the gel during the flow of the sample through the columns. If the gel comes into contact with compounds that can be readily hydrated (*e.g.*, amines), a transitional decrease in the gel pores is observed due to the contact with water molecules, the so-called "trapping effect"[37]. Another factor which greatly contributes to a considerable increase in V_e is the aromatic character of the compounds under investi-

gation. An example can be seen in the behaviour of several aromatic hydrocarbons in Table III. Deviations in the V_e values compared to the assumed molar volumes have been found by Čoupek *et al.*[30]. Since a comparison with a series of amine compounds was necessary, we repeated the measurements under conditions when different absolute V_e values were found. The comparison of relative relationships has confirmed our earlier assumptions; a negative difference between the calculated and the determined molar volumes was observed in all cases under investigation. This is true for both mononuclear and binuclear aromatic hydrocarbons. The aromatics associate with the gel, which is also aromatic; owing to sorption, therefore, they remain in the gel pores much longer than similar non-aromatic compounds. Steric effects also play their part here, especially in the case of bulky substituents.

All the factors outlined above are met in the analysis of aromatic amines. As can be seen from Table II, the minimum deviation between the calculated and effective molar volumes appeared in the case of diphenylamine; here, influences tending to increase and to decrease the molar volume occurred at the same time as result of the presence of two aromatic nuclei and one imino group. The maximum negative deviation was observed for N,N'-di-*sec.*-butyl-*p*-phenylenediamine and N,N'-bis-4-(N,N-dimethylamino)phenyl-*p*-phenylenediamine.

Some basic findings about the effect of the structure of the compounds investigated in this work on the GPC behaviour are as follows. The deviation between the observed and calculated molar volume of benzene was −51.8. Substitution of a benzene ring not containing any solvatable group with small alkyls was reflected in deviations in the range from −23 to −86. Introduction of one –OH or $-NH_2$ group into the benzene ring increases the calculated, as well as the effective, molar volume of benzene by approximately the same value. The deviation between the calculated and the effective molar volume is also comparable. It is interesting to compare the behaviour of the benzene derivatives containing two solvatable groups. The effective molar volumes of *o*- and *p*-aminophenols differ but little from the calculated volume. A high solvation took place in the case of *m*-aminophenol. A similar trend was found in the series of isomeric phenylenediamines. In this case, however, there is a strikingly great difference between the *o*- and *p*-isomers, the latter even exhibiting a negative deviation.

In the case of primary amines with one benzene ring and small substituents in the ring, hydrogen bonds between amine groups and THF can play a specific role. A comparative investigation of the GPC behaviour of selected monoalkylphenols showed that in all cases, even if the less bulky substituent was at position 2, solvation took place. The same holds for 2,4-xylenol. The effective molar volume for all other dialkylphenols analyzed here was the same or smaller than the assumed volume. The effect of the substituent in anilines similarly substituted in the ring with a methyl group was less regular; in particular, a marked difference is seen if 2,4,6-trimethylphenol and 2,4,6-trimethylaniline are compared, for which a similar trend in the solvation effect might have been assumed. An irregular effect on the volume due to solvation can be observed when comparing 2,4,6-trimethylaniline and 2,3,5,6-tetramethylaniline. Less regular influences on the retention time of the substitution of simple aromatic amines, in comparison with phenols, was also observed in column liquid chromatography[41].

The presence of two condensed aromatic nuclei has a strong effect in the

naphthalene series. Introduction of the solvatable group is either virtually not reflected in a decrease in the negative deviation from the calculated molar volume (*cf.*, 2-naphthol), or the solvation makes the effective molar volume only approximate to the calculated volume (both examples were isomeric naphthylamines).

Substitution with one polar group in the diphenyl series (4-phenylphenol) brings the effective molar volume somewhat nearer to the calculated one. The effect of solvation is particularly marked in the presence of two amino groups, as can be seen in the example of benzidine. Experimental data show, however, that hindrance due to a mere methyl group in *o*-toluidine suppresses the effect of solvation in this case.

If the aliphatic substituents are bonded to a nitrogen atom, the possibility of solvation decreases, and the aromaticity of the compound plays the predominant role in the GPC analysis. This fact can be perfectly demonstrated for the series aniline, N-methylaniline and N,N-dimethylaniline. If nitrogen in aniline is substituted by an aromatic residue, a decrease in the observed molar volume can be expected compared to the calculated one, owing to the concurrent effect of the decreased solvation power and increased portion of the aromatic groups. This assumption is fully valid for phenyl-2-naphthylamine or N,N′-bis(4-dimethylamino)diphenylamine, but is not fulfilled for diphenylamine. In accordance with the preliminary data, the presence of a solvatable group in diphenylamine will raise the value of the molar volume observed (*e.g.* 4-aminodiphenylamine). Similarly to the aniline series, a decrease in solvation due to substitution at the nitrogen atom must also be assumed for the phenylenediamine series. From the viewpoint of their activity, the derivatives of *p*-phenylenediamine are of importance; they rank among well-known antioxidants and antiozonants. In the group of aliphatically N,N′-disubstituted derivatives, compounds were studied which differed to a great extent in the volume of the substituent. However, with the exception of compounds substituted with methyl groups (the conclusions hold also for N,N′-dimethyl-2-methyl-*p*-phenylenediamine and N,N,N′-trimethyl-*p*-phenylenediamine) and with *sec.*-butyl, the assumption concerning limited solvation was not fulfilled. Further interactions among molecules of analysed compounds, eluant and gel packing probably occur specifically in the system studied.

A completely anomalous behaviour was exhibited by the N,N′-disubstituted derivatives of *p*-phenylenediamine, in which one of the substituents on the nitrogen atom or both of them were aromatic. For these derivatives, larger elution volumes than those found were assumed, as the aromatic substituents on the nitrogen atom are capable of restricting the formation of hydrogen bonds with THF.

Some of the amine compounds investigated here exhibited negative peaks in refractometric detection, that is, they had a lower refractive index increment than THF, or the shape of the peaks was unusual (Fig. 1). To prevent errors due to an incorrect determination of the peak of a compound, a combination of refractometric and UV detection proved useful.

The purity of commercial samples of amine antioxidants and antiozonants was investigated along with their GPC behaviour. The majority of the derivatives of *p*-phenylenediamine contained various admixtures, which however were present in small amounts only, compared to the main component. Judging by the colour and elution volumes, a part of the impurities consists of oxidation products.

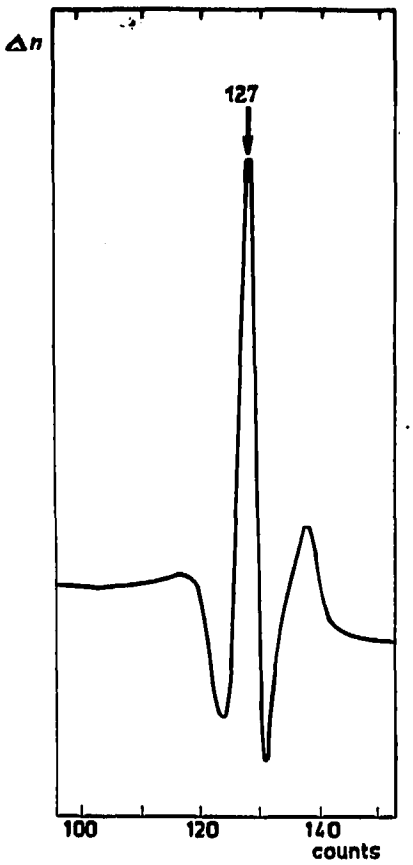


Fig. 1. Chromatogram of N,N,N′-trimethyl-*p*-phenylenediamine: refractometric detection, 1 volume count= 1.98 ml.

CONCLUSION

The investigation revealed the possibility of applying GPC analysis to aromatic amine stabilizers. At the same time, anomalies in behaviour were observed requiring the use of standard compounds in qualitative analysis and a combination with specific colour tests and paper or thin-layer chromatographic methods. The work should be regarded as a basis for analyses of stabilizing systems containing aromatic amines in polyolefinic and rubber materials, and for a study of their oxidative transformations.

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