

## BASIC GEL PERMEATION CHROMATOGRAPHY STUDIES

## II. BENZENE RESULTS WITH SMALL MOLECULES

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## INTRODUCTION

Gel permeation chromatography (GPC) studies from this laboratory have included papers on the elution data from simple solutes in tetrahydrofuran<sup>1</sup> and chloroform<sup>2</sup> using 40 Å gel in the GPC columns. The studies based on tetrahydrofuran led to rules to predict elution, and basically the molecular sizes as seen by GPC were proportional to the sum of the contributing chain lengths. In this early work, hydrogen bonding to the solvent was measured, and almost all non-hindered OH compounds studied were strongly bonded to the solvent. About 130 compounds were studied in tetrahydrofuran, and the correlations used produced a good agreement between a measure of the molecular sizes observed in GPC and the theoretical values for a range of molecular types. The data with chloroform as the solvent showed that it acts as a hydrogen bond donor, and almost no revisions of the concepts used in the tetrahydrofuran work had to be made to explain the chloroform results.

Results in benzene are of interest, since this solvent is classified as neither a hydrogen bond donor or acceptor; yet it is a good GPC solvent and gel swelling agent. An evaluation was also desired as to whether benzene was a rather fine, good or poor choice for studying small molecules, since earlier work could be interpreted either way. CORTIS-JONES<sup>3</sup> studied several solutes and solvents with a range of GPC-type, low permeability gels. From his results with ten oxygenated compounds in benzene, he concluded that the hydroxyl group caused relative exclusion of the compounds that contained this grouping.

## EXPERIMENTAL

Prior techniques were used in this study<sup>1,2</sup>. Basically, 3/8 in. O.D. steel tubing 4 ft. long was packed with 40 Å styrenedivinylbenzene GPC gel. The gel was permeable to alkanes below a molecular weight of 450. The GPC runs were made using a commercial machine, made by Waters Associates Incorporated<sup>4</sup>. Benzene at 1.0 ml/min was the elution solvent, and typically 0.1 ml of 4% solute in benzene was injected using an automatic injection system. Molecular size calibration was based on a mathematical comparison of the elution volume of new solutes to that of the normal alkanes and the ethers studied. The calibration data were fitted to an equation of the form:

$$E = V_x + S \times (\log (\text{No. of C atoms} + R))$$

For atoms other than carbon, their effective chain lengths are given in Table I, using a theoretical model based on additive structural elements. The calibration

TABLE I

A COMPARISON OF EFFECTIVE CHAIN LENGTHS IN GPC  
Based on the elution volumes of *n*-alkanes.

Atoms	Size in tetrahydrofuran (No. of C units)		Size in benzene (No. of C units)		General differences (No. of C units)
	Linear	Pendant	Linear	Pendant	
—CH <sub>3</sub>	1.0	1.0	1.0	1.0	None
C—O—C	0.67	—	0.67	—	None
C=C	1.0	1.0	0.65	0.65	0.35
C=O	0.61	0.61	0	0	0.61
—Cl	1.08	0.43	0.54	0.22	—
—Br	1.37	0.55	0.68	—	—
—I	1.54	—	0.77	—	—
—OH	0.67	0.67	0	0	—
	+2.85 <sup>a</sup>	+2.85 <sup>a</sup>			3.54 <sup>b</sup>
—COOH	2.33	—	—1.5	—	—
	+2.85 <sup>a</sup>		+1.0		5.7 <sup>b</sup>
Ar OH	0.67		—1.5		6.2 <sup>b</sup>
	+4.0 <sup>a</sup>				
—NH <sub>2</sub>	0.91		0		3.76 <sup>b</sup>
	+2.85 <sup>a</sup>				

<sup>a</sup> Hydrogen bonding observed in THF and not in benzene increases molecular size.

<sup>b</sup> Plus a correction of 0.15 times sorbing groups present times length of longest chain.

equations were based on the constants, given in Table II.

In reporting peak widths, tangents were drawn to each side of the GPC curve and the number of milliliters of elution at the base of the triangle is reported in the tables under the heading Elution (ml), at base.

## DISCUSSION

Benzene was studied as a GPC solvent to see if rules could be derived to predict solute elution volumes. As in prior studies, molecular size was determined by com-

TABLE II

CALIBRATION CONSTANTS

Column	$V_x$	S	R	TPF <sup>a</sup>	Length (ft.)
A	98.68	37.14	0.0	500	8
B	165.89	70.88	2.03	990	12
C	137.26	56.06	1.16	990	12
D		(see text)		990	12

<sup>a</sup> Theoretical plates per ft. using *n*-pentane as solute.

TABLE III

THE ELUTION OF NORMAL HYDROCARBONS AND ETHERS IN BENZENE USING 40 Å GPC GEL

Run conditions: 3/8 in. O.D. columns; benzene solvent at 1 ml/min at 24°, using a 12 ft. column, except elution data in parentheses are from an 8 ft. column.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Ob - T)	$C_T - C_B^a$	Column
		To peak	At base	Theory	Obs.			
1	P-4,000	58.3	3.34	—	—	—	—	B
2	( <i>n</i> -C <sub>18</sub> H <sub>37</sub> ) <sub>2</sub> O	62.8	3.60	—	—	—	—	B
3	( <i>n</i> -C <sub>12</sub> H <sub>25</sub> ) <sub>2</sub> O	67.4	3.70	—	—	—	—	B
4	Di-octyl ether	76.0	3.81	16.67	16.50	0.16	—	B
5	<i>n</i> -Dodecane	84.2	3.96	12.0	12.17	0.17	—	B
6	<i>n</i> -Decane	88.9	3.82	10.0	10.16	0.16	—	B
7	<i>n</i> -Heptane	99.2	4.57	7.0	6.69	-0.31	—	B
8	<i>n</i> -Hexane	101.5	3.89	6.0	6.06	0.06	—	B
9	<i>n</i> -Pentane	105.4	3.97	5.0	5.10	0.1	—	B
10	Di-ethyl ether	107.5	4.16	4.67	4.63	-0.04	—	B
11	Di-octyl ether	(53.3)	(4.24)	16.67	16.66	-0.01	—	A
12	<i>n</i> -Dodecane	(58.3)	(4.25)	12.0	12.22	0.22	—	A
13	<i>n</i> -Nonane	(63.0)	(4.20)	9.0	9.13	0.13	—	A
14	<i>n</i> -Heptane	(67.3)	(4.41)	7.0	6.99	-0.01	—	A
15	<i>n</i> -Pentane	(72.4)	(4.48)	6.0	5.10	0.10	—	A
16	Di-ethyl ether	(73.6)	(4.47)	4.67	4.73	0.06	—	A

<sup>a</sup> (Molecular size in tetrahydrofuran) — (the size in benzene in No. of C units).

paring elution volumes of the solutes with a series of normal paraffins and ethers. The results were expressed as an effective chain length of so many carbon atoms long, and the effective length of heteroatoms were figured from their bond lengths, bond angles and covalent radii. Calibration standards are reported in Table III.

Two GPC columns having 8 ft. total length were studied extensively with tetrahydrofuran elution solvent, and then they were studied with benzene solvent. The alkanes and ethers eluted slightly earlier in the new solvent, indicating that benzene was the better gel swelling agent of the two solvents. The ethers and alkanes eluted on the same calibration line, which indicates the absence of partition, adsorption and bonding to the solvent with these ethers. Also, the light gases studied eluted only very slightly after propane, in agreement with the results observed with tetrahydrofuran as the elution solvent. Hence, those compounds eluting after or smaller than a three carbon atom size in the current work were assumed to be sorbed—either adsorbed, absorbed, partitioned, permeated, chemisorbed or otherwise delayed due to contact with the gel surface. Summarizing, sorption played an important role in the elution volumes observed in benzene. The literature on sorption chromatography is developing<sup>5</sup> to show that one can at times predict elutions that are delayed by sorption, and one technique is to predict elution by using factors in a mathematical relationship, which uses one factor for each functional group present. This approach was taken in the current work. However, certain precautions were taken—for example, the degree of steric hindrance of a phenol was a factor in the sorption observed with it, as one might anticipate. Also, sorption was too complex to unravel into its parts at this time.

Benzene derivatives and other aromatic compounds were studied, and their elution volumes were compared to the calibration standards used. A size of 2.2 carbon atoms long was used for the effective size of the phenyl group, and the correlations thus obtained were in good agreement with the observed values, as shown by the data in Table IV.

A group of carbonyl compounds was studied in benzene, and the observed elution volumes deviated from the tetrahydrofuran results—in benzene, these compounds eluted later than the *n*-alkane standards having the same apparent molecular size. However, useful correlations were obtained by not figuring in the oxygen atoms into the chain length. This technique gave the results in Table V. The reasons for this phenomenon are not understood, but sorption appears to play a major role. Nevertheless, these corrections corresponded to only a 10 % to 15 % error in molecular size, which is less than a 5 % change in predicted elution volumes.

A group of halogenated compounds also eluted later in benzene than in tetrahydrofuran, but not very much later. As expected, chloroform appeared later and hence smaller than did carbon tetrachloride in benzene. Since no molecule looked bigger than expected, one may conclude that there was no evidence for hydrogen bonding of these compounds or for self-association in benzene. Correlations were tried on the data, and the one that appeared to work best was to place a value on each halide atom at half of the size found in the tetrahydrofuran work. This data is compared in Table I, and the observed results using these chain lengths are given in Table VI. The results agree fairly well with the theory.

A group of alcohols and amines were studied in benzene to detect their elution pattern. An initial tabulation of the data for the alcohols indicated also that the oxygen

TABLE IV  
THE ELUTION OF AROMATIC HYDROCARBONS AND ETHERS IN BENZENE USING 40 Å GPC GEL  
Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Ob - T)	C <sub>T</sub> - C <sub>B</sub>	Column
		To peak	At base	Theory	Obs.			
1	Toluene	( 81.0	— )	3.20	2.99	-0.20	1.09	A
2	Ethylbenzene	( 75.2	— )	4.20	4.28	0.08	0.56	A
3	<i>p</i> -Xylene	( 76.2	— )	4.20	4.02	-0.18	0.58	A
4	Cumene	( 71.0	— )	5.20	5.56	0.36	0.33	A
5	Naphthalene	( 81.5	6.20)	3.18	2.90	-0.28	1.29	A
6	Biphenyl	( 75.2	5.92)	4.40	3.95	-0.45	1.49	A
7	Diphenylmethane	102.7	5.08	5.40	5.40	0.0	—	B
8	Diphenoxyethane	96.0	4.94	7.73	7.65	-0.08	1.76	B
9	Dicumyl peroxide	84.8	6.02	11.73	11.90	0.17	0.76	B
10	Anisole	114.6	4.56	3.87	3.26	-0.61	0.94	B
11	Phenetole	107.6	4.43	4.87	4.61	-0.26	—	B

TABLE V  
 THE ELUTION OF CARBONYL COMPOUNDS IN BENZENE USING 40 Å GPC GEL  
 Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No of C units)		Error (Ob - T)		C <sub>T</sub> - C <sub>B</sub>	Column
		To peak	At base	Theory	Obs.	$\Delta$	$\Delta\Delta$		
1	Acetone	( 78.6	4.66)	3.0	3.47	0.47		0.66	A
2	Acetone	115.3	4.34	3.0	3.19	0.19		0.94	B
3	Acetone	101.5	4.52	3.0	3.18	0.18		0.95	C
4	<i>n</i> -butyraldehyde	110.4	4.46	4.0	4.03	0.03			B
5	2-Butanone	110.3	4.10	4.0	4.05	0.05		0.71	B
6	Ethyl acetate	108.6	4.34	4.0	4.39	0.39			B
7	Isobutyl methyl ketone	102.2	4.40	6.0	5.88	-0.12			B
8	Dimethyl terephthalate	100.6	5.30	6.2	6.30	0.10			B
9	<i>n</i> -Heptaldehyde	98.1	6.40	7.0	7.01	0.01			B
10	Dimethyl adipate	94.2	4.17	8.0	8.23	0.23			B
11	Dimethyl sebacate	73.8	4.62	12.0	12.39	0.39			C

TABLE VI

THE ELUTION OF ORGANIC HALIDES IN BENZENE USING 40 Å GPC GEL

Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)	Error (Ob - T)		C <sub>T</sub> - C <sub>B</sub>	Column
		To peak	At base		Δ	ΔΔ		
1	Methyl iodide	( 88.3	( — )	1.77	1.90	0.13	0.55	A
2	Ethyl bromide	( 81.9	( 5.18)	2.68	2.85	0.17	0.54	A
3	Chloroform	( 82.3	( 5.70)	2.51	2.76	0.25	2.15	A
4	Carbon tetrachloride	( 80.0	( 5.70)	2.74	3.18	0.44	1.29	A
5	Ethylene dichloride	( 80.8	( 5.28)	3.09	3.02	-0.06		A
6	Methylchloroform	( 77.8	( 5.44)	3.20	3.64	0.44		A
7	Tetrachloroethane	( 78.0	( — )	3.51	3.60	0.09	5.16	A
8	Pentachloroethane	( 77.0	( — )	3.61	3.83	0.22	3.26	A
9	Perchloroethane	( 77.6	( — )	4.04	3.69	-0.35	1.63	A
10	1,4-Dichlorobutane	( 74.0	( — )	5.09	4.61	0.07	1.52	A
11	Benzene hexachloride	( 70.7	( — )	(5.29)	5.66	0.37)		A
12	Chlorobenzene	( 80.6	( 5.28)	2.74	3.06	0.32	1.38	A
13	Bromobenzene	( 81.7	( 5.45)	2.88	2.86	-0.02	1.42	A
14	Iodobenzene	( 81.7	( 5.80)	2.97	2.86	-0.11	1.41	A
15	Dibromobenzene-( <i>p</i> )	103.9	4.85	3.57	2.89	-0.68		C
16	Dichlorobenzene-( <i>p</i> )	102.0	4.93	3.29	3.22	-0.07		C

TABLE VII  
THE ELUTION OF ALCOHOLS IN BENZENE USING 40 Å GPC GEL  
Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Ob - T)	$C_T - C_B$	Column
		To peak	At base	Theory	Obs.			
1	Methanol	(92.0)	5.47)	1.0	1.51	0.51	5.08	A
2	Ethanol	127.3	4.54	2.0	1.45	-0.55	4.33	B
3	Isopropyl alcohol	117.6	4.52	3.0	2.76	+0.06	4.13	B
4	<i>n</i> -Propanol	(81.3)	5.47)	3.0	2.93	-0.07	3.64	A
5	Benzyl alcohol	(82.7)	5.22)	3.2	2.69	-0.51		A
6	<i>tert</i> -Butyl alcohol	110.7	4.60	4.0	3.97	-0.03		B
7	<i>n</i> -Butanol	112.7	4.82	4.0	2.97	-1.03		B
8	3-Heptanol	(68.7)	4.65)	7.0	6.41	-0.59	3.75	A
9	<i>n</i> -Heptanol	(69.8)	4.77)	7.0	5.99	-1.01	4.30	A
10	<i>n</i> -Heptanol	101.0	4.40	7.0	6.20	-0.80	4.09	B
11	Diethylene glycol monomethyl ether	97.3	4.88	7.0	6.33	-0.67		B
12	2,2,4-Trimethylpentanol	98.7	4.70	8.0	6.83	-1.17		B
13	<i>n</i> -Decanol	93.5	4.70	10.0	8.47	-1.53	5.11	B
14	<i>n</i> -Decanol	82.2	4.51	10.0	8.43	-1.57		C



TABLE VIII

THE ELUTION OF AMINES IN BENZENE USING 40 Å GPC GEL

Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Ob - T)	C <sub>T</sub> - C <sub>B</sub>	Column
		To peak	At base	Theory	Obs.			
1	Aniline	128.8	7.24	2.2	1.39	-0.81	5.27	B
2	Aniline	(86.6)	(6.57)	2.2	2.11	-0.09	4.57	A
3	Pyridine	(84.6)	(6.76)	2.2	2.39	0.19	0.90	A
4	Benzylamine	(83.5)	5.53)	3.20	2.56	-0.63	-0.15	A
5	Dimethylamine	110.0	5.40	4.20	4.11	-0.09		

TABLE IX

THE ELUTION OF PHENOLS IN BENZENE USING 40 Å GPC GEL

Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Ob - T)	C <sub>T</sub> - C <sub>B</sub>	Column
		To peak	At base	Theory	Obs.			
1	Phenol	125.0	6.25	2.2	0.72	-1.48	6.81	D
2	<i>p</i> -Cresol	129.3	6.13	3.2	1.25	-1.95		B
3	<i>p</i> - <i>tert</i> -Butylphenol	101.9	6.16	6.2	3.70	-2.49		D
4	Bisphenol "A" ( <i>p,p'</i> )	(76.2)	12.95)	7.4	4.02	-3.37	0.29	A
5	Bisphenol "A" ( <i>p,p'</i> )	117.7	8.37	7.4	2.75	-4.65	-0.99	B
6	<i>o,p'</i> -Bisphenol "A"	110.0	6.97	7.40	4.11	-3.28	0.05	B
7	2,6-Diisopropylphenol	95.5	—	8.20	7.81	-0.39	-0.39 <sup>a</sup>	B
8	6,4,6',4'-Tetramethyl-2,2'-dihydroxybiphenyl	89.9	4.52	8.40	6.80	-1.60	0.38 <sup>a</sup>	D
9	4,6,4',6'-Tetra- <i>tert</i> -butyl-2,2'-dihydroxybiphenyl	64.9	6.23	20.4	18.37	-1.63	0.47 <sup>a</sup>	D

<sup>a</sup> One OH group is sterically hindered.

atom of the OH groups could be ignored in measuring the effective chain length, as was done with the ketones and esters studied. However, a slightly larger correction was needed for the alcohols than was made for the carbonyl compounds. Plotting the data led to the conclusion that a correction of 0.15 carbon atoms chain length times the length of the longest chain length attached to the OH group gave an improved correlation. Further, it was observed that this correction peaked out at about 10 carbon atoms and declined thereafter. These results are tabulated in Table VII, and the refined results are compared to the observed values in the column of Table VII headed by the symbols  $\Delta\Delta$ . Amines also conformed to this general picture, with some reservations. The nitrogen of the amine could be ignored from measurements of the effective chain length in benzene, provided that it was not buried, such as in nitrobenzene or diethylaniline. The 0.15 carbon atoms correction for the longest chain also appeared to be applicable to the amines, although this is based on a relatively small number of tests. These results with amines are given in Table VIII.

With phenols in benzene, elution occurred much later than in tetrahydrofuran, and the difference was typically about seven carbon atoms in size. This would consist of four carbon atoms length due to the absence of hydrogen bonding, 0.65 C units due to the smaller effect of the aromatic ring in determining molecular size, 0.65 C units due to not measuring the oxygen atom, and about 1.5 carbon atoms length beyond these factors. With the substituted phenols, elution was still later than was anticipated with the above four corrections applied to phenols, and the delay paralleled that observed with alcohols. Hence an 0.15 C units times the chain length correction has also been figured into the revised chain lengths for the phenol data, and the results in Table IX agree closely with the observed values.

Organic acids in benzene were also studied, and the results indicated a high degree of sorption. Typically, the portion of the GPC curve that eluted first was very close to normal in shape and width, for organic acids in benzene; but these acids eluted over a range of 15 to 25 ml, which was several fold more than the other solutes of the current study. Also, the elution position of the acids changed considerably from column to column, and the position of elution was changed by other polar solutes present. For example, acetic acid eluted 5 ml earlier in the presence of phenol, compared to when it was injected alone. Still, rules were sought to predict the elution of these acids studied. The elution correlations finally chosen were in line with the prior observations. The oxygen atoms were not figured into the effective chain lengths, and a correction of 1.5 carbon atoms lengths was applied for the acidic hydrogen present. Further, a correction of 0.3 carbon atoms per carbon atom in the longest chain attached to the COOH group appeared appropriate. (One may reason that the COOH group is a bidentate type of absorbing group). Using these guidelines, the results in Table X were obtained, and the agreement of theoretical and observed values was fairly good.

Epoxides were also studied, and in this case the best correlations were obtained by combining two prior principles; these were not to figure in the oxygen in a group that could be sorbed and to subtract 0.67 C units for the small ring structure. These concepts led to the results in Table XI. A group of other cyclic compounds were studied, and they gave results in line with the molecular sizes observed in tetrahydrofuran. These results are also given in Table XII.

In tetrahydrofuran, unsaturated compounds showed almost no deviation from

TABLE X

THE ELUTION OF ORGANIC ACIDS IN BENZENE USING 40 Å GPC GEL

Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Ob - T)	C <sub>T</sub> - C <sub>B</sub>	Column
		To peak	At base	Theory	Obs.			
1	Acetic acid	131.7	20.5 <sup>a</sup>	2.0	0.27	-1.72	5.95	B
2	Caproic acid	115.6	23.4 <sup>a</sup>	6.0	3.10	-2.90		B
3	Heptanoic acid	112.2	18.6 <sup>a</sup>	7.0	3.69	-3.31		B
4	Palmitic acid	80.3	15.1 <sup>a</sup>	16.0	14.09	-1.90		B

<sup>a</sup> Considerable tailing was observed, and the width of the leading edge was similar to that of other compounds studied.

TABLE XI

THE ELUTION OF EPOXIDES IN BENZENE USING 40 Å GPC GEL

Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Ob - T)	C <sub>T</sub> - C <sub>B</sub>	Column
		To peak	At base	Theory	Obs.			
1	Propylene oxide	119.7	4.41	3.0	2.46	-0.54	0.57	B
2	Phenyl glycidyl ether	106.4	5.07	5.87	4.87	-1.00		B
3	Butyl glycidyl ether	97.6	4.56	7.67	7.16	-0.51		B
4	<i>p,p'</i> -Bisphenol diglycidyl ether	82.3	5.69	14.41	13.40	-1.01		B

TABLE XII

THE ELUTION OF CYCLIC, UNSATURATED, AND BRANCHED COMPOUNDS IN BENZENE USING 40 Å GPC GEL

Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Obs - T)	C <sub>T</sub> - C <sub>B</sub>	Column
		To peak	At base	Theory	Obs.			
1	Tetrahydrofuran	113.4	4.75	2.85	3.47	0.62		B
2	Cyclohexane	110.7	4.59	3.40	3.97	0.57	0.05	B
3	Cyclohexane	( 76.2	5.44)	3.40	4.02	0.62	0.10	A
4	Furan	112.9	4.90	2.85	1.93	-0.92		D
5	Furan	107.1	4.78	2.85	2.29	-0.54	0.26	C
6	Allyl alcohol	110.0	5.11	2.55	1.90	-0.65	-0.25	C
7	2-Butene-1-ol	103.8	5.30	3.40	2.92	-0.48	-0.08	C
8	Propargyl chloride	108.8	4.90	3.43	2.06	-1.37	(-0.57)	C
9	Phenylacetylene	( 79.2	5.67)	4.10	3.34	-0.76	(0.04)	A
10	Styrene	114.2	4.82	4.10	3.33	-0.77	-0.37	B
11	2-Methylpentene-1	91.8	4.85	6.0	5.31	-0.69	-0.29	B
12	4-Methylpentene-1	90.6	4.21	6.0	5.63	-0.37	0.03	B
13	Heptene-1	( 67.3	4.41)	7.0	6.53	-0.46	-0.06	A
14	Decene-1	82.7	4.56	10.0	9.54	-0.45	-0.05	D
15	Isooctane	( 65.6	4.28)	8.0	7.77	-0.23		A

TABLE XIII

THE ELUTION OF MISCELLANEOUS COMPOUNDS IN BENZENE USING 40 Å GPC GEL

Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Ob. - T)		$C_T - C_B$	Comments and column
		To peak	At base	Theory	Obs.	$\Delta$	$\Delta\Delta$		
1	Ionol	( 60.4	5.79)	11.2	11.0	-0.2		0.63	A <sup>b</sup>
2	Triphenylcarbinol	( 65.8	— )	7.6	7.67	0.07		4.60	A
3	Propylene carbonate	( 76.5	5.47)	4.0	3.9	-0.1			A
4	Nitroethane	( 79.8	— )	2.9	3.22	0.32			A <sup>c</sup>
5	Nitrobenzene	( 79.5	5.58)	3.1	3.29	0.19		2.17	A <sup>c</sup>
6	Nitrobenzene	116.0	4.75	3.1	3.02	-0.08		2.34	B <sup>c</sup>
7	Acetonitrile	( 84.5	5.04)	2.0	2.40	0.40		0.5	A <sup>d</sup>
8	Propionitrile	115.4	4.78	3.0	3.12	0.12			B <sup>d</sup>
9	Hexanonitrile	100.4	4.20	6.0	6.36	0.36			B <sup>d</sup>
10	Adiponitrile	102.8	4.23	6.0	5.73	-0.27			B <sup>d</sup>
11	Dipropylene glycol	( 68.1	7.16)	6.67	6.65	-0.02		4.98	A <sup>d</sup>
12	Tripropylene glycol	( 61.8	5.36)	10.33	9.84	-0.49		4.85	A <sup>d</sup>
13	Tetraethylene glycol	86.7	4.77)	10.0	11.06	1.06	0.39		B <sup>d</sup>
14	Hydrogenated bisphenol "A"	96.1	7.63	8.54	7.62	-0.92	0.24		B <sup>d</sup>
15	n-Propyl sulfide	92.6	4.96	6.0	5.96	-0.04			D <sup>d</sup>
16	Carbon disulfide	134.7	4.72	1.0	0.72	-0.28			B <sup>d</sup>
17	Diethyl carbonate	102.8	4.23	5.0	5.73	0.73	0.06		B <sup>d</sup>

<sup>b</sup> Buried OH group. <sup>c</sup> Buried N atom. <sup>d</sup> See text.

TABLE XIV

THE ELUTION OF OTHER COMPOUNDS IN BENZENE USING 40 Å GPC GEL

Run conditions: see Table III.

Run	Compound	Elution (ml)		Compared chain length (No. of C units)		Error (Ob. - T)	C <sub>T</sub> - C <sub>B</sub>	Column
		To peak	At base	Theory	Obs.			
1	<i>p</i> -Methoxyphenol	139.8	5.60	1.79	0.30	-1.49		B
2	Quinoline	126.2	6.45	3.18	1.59	-1.59		B
3	Methyl methacrylate	98.2	4.95	4.65	3.81	-0.84		C

the size of the corresponding saturated compounds, but in benzene solvent the unsaturated structure appeared to change the molecular size consistently by about 0.35 carbon atom units. Thus heptene-1 appeared only 6.65 carbon atoms long in benzene. There was some scatter to the data, but there was general agreement with this value, even among the more polar compounds. An interesting case is  $\phi-N=N-\phi$ , which has an effective chain size of 4.06 carbon atoms long *vs.* 4.05 calculated. Acetylenic unsaturation also briefly studied. The aliphatic acetylenic compounds studied appeared to be about 1.5 C units smaller than their saturated analogues, and the correction factor was 0.75 C units smaller with phenylacetylene, a single example of an aromatic acetylenic compound.

The relatively few adjusting factors in this report did not allow quite all the data to give high quality correlations, although further correction factors may be needed. In almost all of these deviating results, one observes changes in sorption due to the presence of additional polar or semi-polar sites. These examples are given in Tables XIII and XIV. However, an attempt is made to interpret Table XIII and some of the deviations in light of other observations in this report, or in most cases an attempt was made to determine the basic process that lead to changes in anticipated elution volumes in the current work. Ionol (2,6-di-*tert.*-butyl-*p*-cresol) gave the expected elution, as did triphenylcarbinol and propylene carbonate. The nitrogen atoms of nitroethane and nitrobenzene were buried, in position, but they were effective in determining the effective GPC chain lengths in benzene. The nitrogen atoms of the nitriles studied did not contribute to the effective GPC chain lengths, which parallels results with the non-hindered amines studied. In the propylene glycol series, no correction of 0.15 times the lengths of the longest chain needed to be made; probably this reflected that the small propylene glycol homologues are not gel swellers and they are probably repelled from the gel surface in benzene. Similarly, no correction for sorption was needed with tetraethylene glycol in benzene in these GPC studies. In contrast, hydrogenated bisphenol "A" was smaller than one might initially anticipate, and the correction of 0.30 times the longest chain appeared applicable, as one might presume necessary for a bidentate compound. Sulfur atoms did not commonly contribute to the effective chain length of the compounds in the current study, as judged for example by comparing *n*-propyl sulfide with *n*-hexane; both eluted at close to the same elution volume. Further evaluation of the esters studied herein lead to the assumption that the ethereal oxygen of this group may be as much as 50% effective in determining effective GPC size in benzene. Further evaluations appear desirable for these compounds.

A few compounds did not elute in benzene as early as one might predict from their revised chain lengths. In general, this was due to the presence of more than one polar and/or aromatic sites close together in the same molecule. The examples observed were methyl methacrylate, quinoline, *p*-methoxyphenol, and  $\beta$ -ethoxyethanol. While the GPC size of these compounds was predicted with an error of 20%, the elution volume was in general predicted with an error of 10% or less.

One should also be on guard for a shift in calibration curve with benzene solvent and the GPC gels such as those used in this study. The calibration of columns B and C represent different curves with the same columns. Column D is also physically the same column as B and C, where only a few of the desired calibration points were available due to not realizing the likelihood of the change. In this case, the  $V_x$  term

for column D appeared to be 3.16 ml less than for column C, and even a bigger difference was observed between columns B and C. The contributing factors to calibration change include aging, major changes in the solvent or samples reaching the columns, and connecting and reconnecting to install the columns in the GPC system.

#### SUMMARY

Elution volumes in gel permeation chromatography have been examined for 90 compounds using benzene as the elution solvent. Sorption to a degree was observed with almost all the aromatic and oxygenated compounds studied. Thus, elution volumes increased in the order *n*-heptane < *n*-heptaldehyde < *n*-heptyl alcohol < 3-heptanol < *n*-heptanoic acid. After *n*-heptanoic acid, toluene and then *p*-cresol eluted, indicating the separation of aromatic from non-aromatic compounds having the same number of carbon atoms.

Rules were proposed for predicting elution volumes for solutes in benzene with the 40 Å gel permeation chromatography gel. There was a good correlation between observed and theoretical values.

#### REFERENCES

- 1 J. G. HENDRICKSON AND J. C. MOORE, *J. Polymer Sci.*, A-1-4 (1966) 167.
- 2 J. G. HENDRICKSON, paper presented at the *Fourth International GPC Symposium, Miami Beach, Fla., May 21st, 1967*.
- 3 B. CORTIS-JONES, *Nature*, 191 (1961) 272.
- 4 L. E. MALEY, *J. Polymer Sci.*, 8C (1965) 243.
- 5 L. R. SNYDER, *J. Chromatog.*, 23 (1966) 388.

*J. Chromatog.*, 32 (1968) 543-558