

CHROM. 5124

## GEL PERMEATION CHROMATOGRAPHIC ELUTION BEHAVIOR OF BRANCHED ALKANES

W. W. SCHULZ

*Esso Research and Engineering Company, P.O. Box 121, Linden, N.J. 07036 (U.S.A.)*

## SUMMARY

The conformation of a branched alkane molecule can be described by the average number of gauche arrangements ( $Zg$ ) which the molecule can assume. A quantitative relation of great exactness has been shown to exist between  $Zg$  and such bulk properties of branched alkanes as refractive index, density and heat of combustion.

The present study extends  $Zg$ -related properties to include gel permeation chromatographic elution behavior of branched alkanes in the range of  $C_7-C_{11}$ . The same simple rules, which had been evolved earlier for precise calculations of refractive index values, can be employed to predict gel permeation chromatographic elution behavior via the molecular volume concept.

The results of the study further confirm that the gel permeation process is one of volume exclusion and that for small, non-polar molecules a description of molecular volume is apparently sufficient to explain elution behavior.

## INTRODUCTION

The conformation of a branched alkane can be described by the average number of gauche arrangements ( $Zg$ ) which the molecule can assume. A method for calculating  $Zg$ -values has been published and applied to the calculation of  $Zg$ -values of over one hundred singly and doubly branched alkanes<sup>1,2</sup>.

A linear dependence of great exactness was observed between  $Zg$ -values and such bulk properties of branched alkanes as refractive index, density and heats of combustion. It was found that the increment in physical property values, which each gauche conformation affects, is constant for all isomeric hydrocarbons and inversely proportional to molecular weight for alkanes of different carbon numbers. The introduction of an additional tertiary carbon atom in the hydrocarbon chain produces a constant shift, equivalent to one gauche conformation. For doubly branched alkanes steric effects require correction terms. However, these corrections were found to be systematic and applicable to all analogously branched alkanes.

The observed correlations were taken as confirmation of the quantitative relation that exists between molecular volume and conformation. The fact that each gauche conformer exerts an identically large effect on such bulk properties as density,

refractive index and heat of combustion was taken as evidence that the properties are primarily dependent on intra-molecular interactions; while properties, such as boiling point or gas chromatographic retention index, would presumably be more responsive to inter-molecular interactions and would not be expected to correlate. The absence of correlations between  $Z_g$ -values of singly branched tridecane isomers and their experimentally determined boiling points or gas chromatographic retention indices was taken as support for this reasoning<sup>2</sup>.

In contrast to gas chromatography, which is based on a gas/liquid partition process, gel permeation chromatography (GPC) is believed to operate by molecular volume exclusion from a porous stationary phase. For macromolecules, hydrodynamic volume or mean external length are molecular size parameters which successfully correlate size and GPC elution volume for a number of polymers<sup>3-5</sup>. For small molecules, HENDRICKSON AND MOORE<sup>6</sup> and HENDRICKSON<sup>7</sup> related GPC elution volume of a large number of hydrocarbons and substituted hydrocarbons to their extended chain length values. SMITH AND KOLLMANSBERGER<sup>8</sup> noted an improved correlation using molar volume rather than chain length for hydrocarbons and halogenated aromatic compounds. Similarly, CAZES AND GASKILL<sup>9</sup> found molar volume correlative with GPC retention volume for a number of small molecule hydrocarbons, acids and alcohols. The GPC behavior of more than a hundred polynuclear aromatic hydrocarbons<sup>10</sup> indicated that separation is a complex function of molecular size, shape and polarity with no readily apparent correlations. From a GPC study of phenyl- and benzo-substituted aromatic compounds, it was concluded that the more molecular dimensions are considered, the more accurately the elution volume can be predicted, and that a sufficient number of molecular dimensions may uniquely describe the elution volumes of a small group of compounds<sup>11</sup>.

The feasibility of extending the existing correlations between molecular conformation and molecular volume of branched hydrocarbons to include GPC elution behavior was studied with the aim of finding systematic correlations between size, structure and GPC elution volume of small molecules. Such correlations would provide additional insight into GPC's separation mechanism, aid in the prediction of the elution behavior or structure of unknown hydrocarbons, and be helpful towards the quantitative evaluation of chromatograms of saturated hydrocarbon oligomers and low-molecular-weight polymers.

## EXPERIMENTAL

### *Apparatus and procedure*

All measurements of elution volume were performed by means of Waters' Gel Permeation Chromatograph Model 100, employing an R-4 type differential refractometer detector. Four 4-ft. columns in series were used with nominal pore sizes of  $10^4$  Å,  $10^3$  Å,  $10^2$  Å,  $10^2$  Å. A total plate count of 1178 P/ft. was determined, injecting dichlorobenzene and applying the usual procedure for chromatogram width measurement and plate count calculation. Elution volumes were measured at peak maxima.

The solvent was tetrahydrofuran and the instrument temperature 23°. Samples were manually injected for 10-15 sec as 0.25 wt. % solutions in tetrahydrofuran. Solvent flow rate was kept close to 1 ml/min and detector sensitivity at  $4 \times$ . All elutions were performed in close succession over a 3-day period to minimize the possibility

of column performance or calibration changes.  $Z_g$ -values and corrections for double branching were obtained from tables published by MANN and coworkers<sup>1,2</sup>.  $Z_g$  corrections were introduced to refer all double-branched alkanes to a single-branch basis for comparison purposes.

### Materials

Hydrocarbons were either API standards or purchased from the Chemical Samples Company. Tetrahydrofuran was obtained from Matheson Coleman & Bell and used without further purification.

TABLE I

ELUTION VOLUMES, AVERAGE NUMBER OF GAUCHE ARRANGEMENTS ( $Z_g$ ) AND CALCULATED MOLAR VOLUMES OF BRANCHED ALKANES

Compounds	Elution volume (counts)	$Z_g$	$Z_g$ corrections for double branching			Corr. $Z_g$	Molar volume
			Add. branch	1,1	1,2		
3-Ethylpentane	30.58	3.58				3.58	143.5
3-Methylhexane	30.30	2.47				2.47	145.8
2-Methylhexane	30.13	1.64				1.64	147.6
2,4-Dimethylpentane	30.05	2.00	-0.88		-0.11	1.01	149.0
3,3-Dimethylpentane	30.38	4.00	-0.88			3.12	144.5
2,3-Dimethylpentane	30.43	3.55	-0.88		+0.60	3.27	144.1
2-Methyl-3-ethylpentane	30.07	5.00	-0.88		+0.64	4.76	158.8
4-Methylheptane	29.85	2.65				2.65	162.1
3-Methylheptane	29.87	2.79				2.79	161.8
2,5-Dimethylhexane	29.59	2.34	-0.88			1.46	164.6
2,2-Dimethylhexane	29.61	2.38	-0.88	+0.14		1.64	164.2
2,4-Dimethylhexane	29.80	3.23	-0.88		-0.20	2.19	163.1
3,3-Dimethylhexane	29.92	4.00	-0.88	+0.14		3.26	160.9
2,3-Dimethylhexane	29.94	3.74	-0.88		+0.64	3.50	160.4
2-Methylheptane	29.71	1.93				1.93	163.6
2,2-Dimethylheptane	29.19	2.66	-0.88	+0.20		1.98	180.2
2,4-Dimethylheptane	29.35	3.38	-0.88		-0.20	2.30	179.6
2,6-Dimethylheptane	29.22	2.59	-0.88			1.71	180.7
3,5-Dimethylheptane	29.47	4.47	-0.88		-0.20	3.39	177.4
4,4-Dimethylheptane	29.54	4.00	-0.88	+0.20		3.32	177.7
3,3-Dimethylheptane	29.49	4.38	-0.88	+0.20		3.70	177.0
3-Ethylheptane	29.58	4.08				4.08	176.3
2-Methyloctane	29.23	2.22				2.22	179.9
3-Methyloctane	29.38	3.08				3.08	178.2
4-Methyloctane	29.41	2.97				2.97	178.6
4-Methylnonane	28.99	3.26				3.26	194.4
3-Methylnonane	29.05	3.38				3.38	194.2
2-Methylnonane	28.93	2.52				2.52	195.8
5-Ethylnonane	28.77	4.57				4.57	208.9
4-Methyldecane	28.60	3.56				3.56	210.7
3-Methyldecane	28.58	3.68				3.68	210.5
2-Methyldecane	28.60	2.82				2.82	212.1

## RESULTS AND DISCUSSION

*Elution volume correlations*

Table I lists all measured elution volumes and calculated  $Zg$ -values as well as molar volumes. A plot of molar volume against  $Zg$ -values for all hydrocarbons studied results in a series of straight-line parallel curves, with a separate curve for each group of isomers (Fig. 1). The fact that the curves are of equal slope and equidistant from

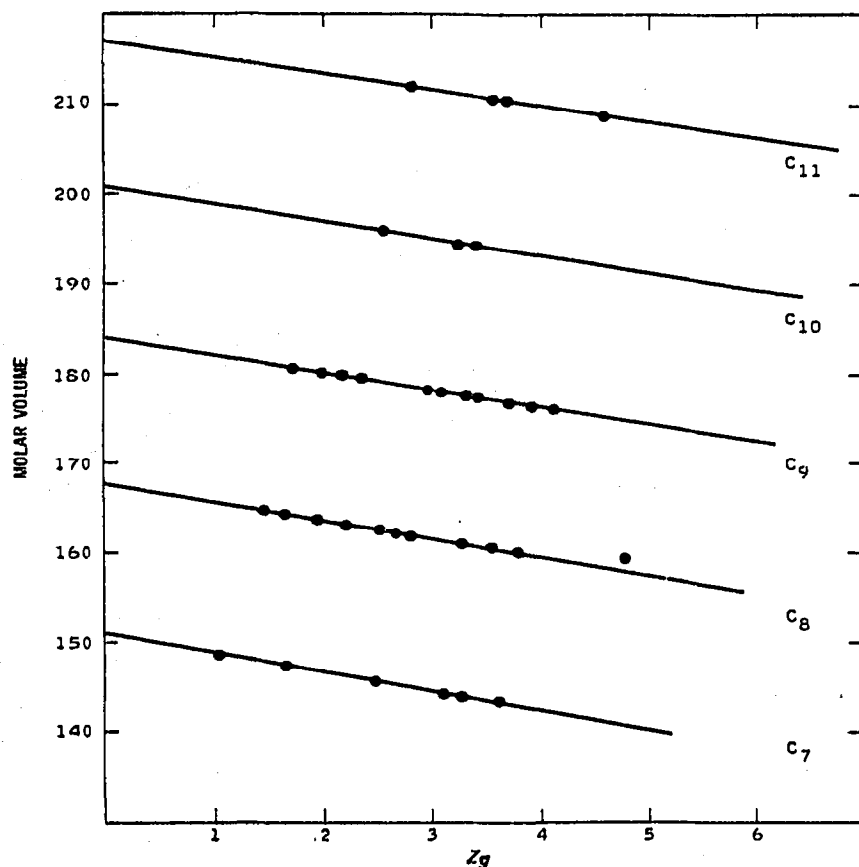


Fig. 1. Correlation of molar volume with average number of gauche conformers ( $Zg$ ) and carbon number.

each other indicates that the contributions of carbon number and  $Zg$  to molar volume are independent and constant. The contribution of carbon number is 7.5 times greater than the conformational contribution. The plotted  $Zg$ -values have been adjusted to a comparable single-branch basis, using literature correction values for double branching<sup>2</sup>.

The interdependence of molar volume ( $V_m$ ),  $Zg$ , and carbon number ( $C$ ) can be expressed in the following equation

$$V_m = aZg + b \cdot C + c \quad (1)$$

The values of the constants were measured to be  $a = -2.22$ ,  $b = 16.5$  and  $c = 35.8$ .  $V_m$  is expressed in units of ml/mole.

Similarly, a plot of  $\log Zg$  against GPC elution volume ( $V_e$ ) presents a family

of linear curves which exhibit the same carbon number groupings and approximately equidistant shifts (Fig. 2). The data are not of a sufficiently wide range and precision to distinguish experimentally between equidistant spacings or spacings that

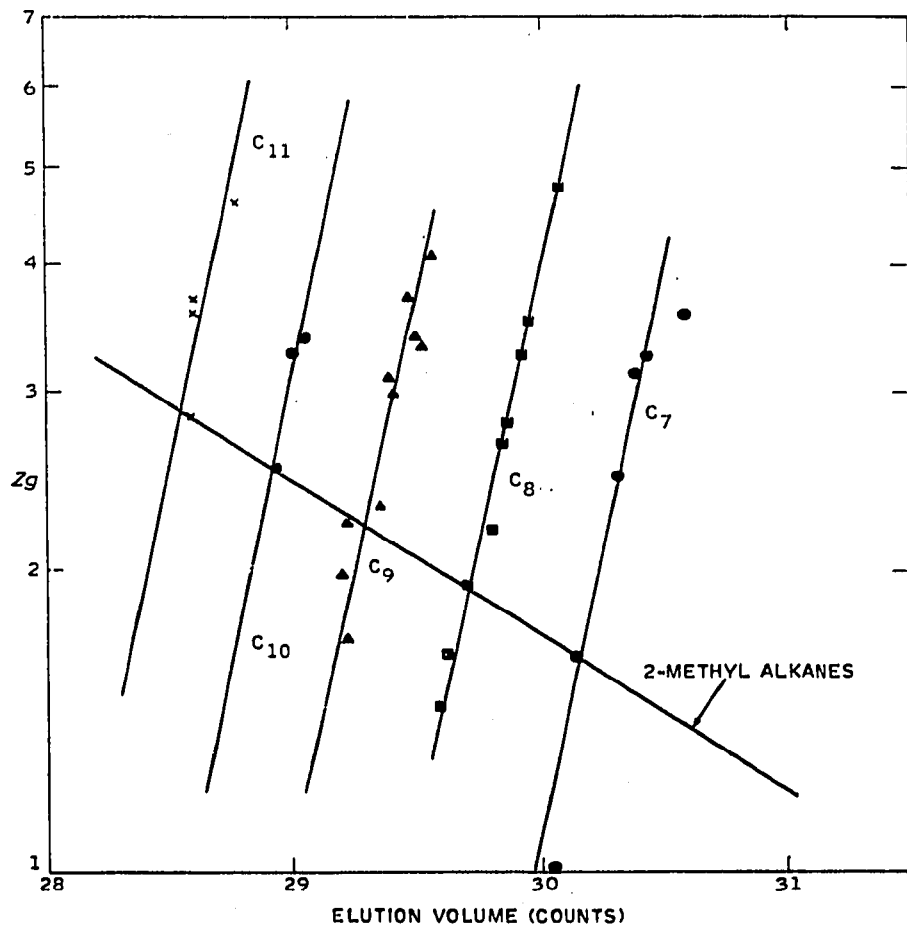


Fig. 2. Correlation of average number of gauche conformers ( $Z_g$ ) with GPC elution volume.

vary logarithmically with carbon numbers. The relation between  $V_e$ ,  $Z_g$  and  $C$  might be expressed in the following form:

$$V_e = a' \log Z_g + b' \log C + c' \quad (2)$$

The experimental values for the constants are:  $a' = 1.0$ ,  $b' = 9.3$ ,  $c' = 37.8$ .

If for any group of compounds one of the independently contributing factors of  $Z_g$  and  $C$  can be related to the other, molar volume or GPC elution volume becomes a function of only  $Z_g$  or  $C$ . Such is the case for a homologous series, for which the change in  $Z_g$  with  $C$  appears to be constant. As an example, the increase of  $Z_g$  for an additional methylene group for the 2-methyl branched hydrocarbon series is 0.30. Eqn. 2 reduces now to a linear variation of  $V_e$  with  $\log Z_g$ . Experimental data for this series verify the prediction (Fig. 2). Alternately, a linear relation of  $V_e$  with  $\log C$  (or molecular weight) would be expected. This is a familiar relation having been demonstrated many times before. It seems to be fundamental to the GPC separation process, holding true over a molecular weight range in which columns fractionate with equal efficiency.

The derivation of eqns. 1 and 2 was undertaken preliminary to relating  $V_e$  with  $V_m$ . The earlier equations predict  $V_e$  to be dependent on molar volume and carbon numbers. The prediction is borne out by the experimental data. Plots of  $V_e$  vs.  $\log V_m$  result in the familiar group of isomeric compound curves (Fig. 3).

$$\log V_m = a''V_e + b'' \log C + C'' \quad (3)$$

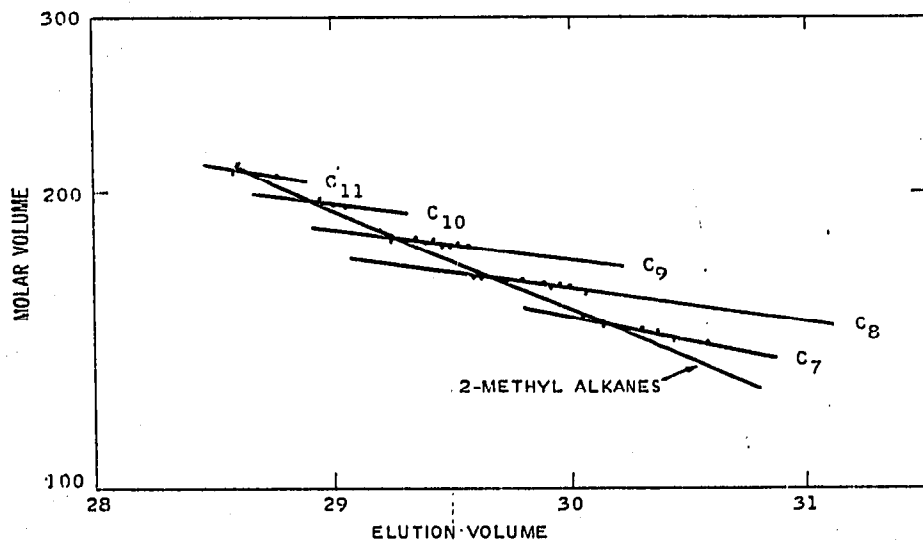


Fig. 3. Correlation of molar volume with GPC elution volume.

Again, the separate contributions of conformation and carbon number are visible from the group of curves. For the 2-methyl branched homologous series  $V_e$  varies linearly with  $\log V_m$  (Fig. 3). The construction of a calibration curve, common to all hydrocarbons investigated, was attempted by parallel shifting of all isomeric curves to a common line (Fig. 4). The shifts amounted to a value of  $\log 12$  or multiples thereof.

The conclusion is that molar volume alone does not uniquely describe elution behavior of branched hydrocarbons unless carbon number is also considered. How-

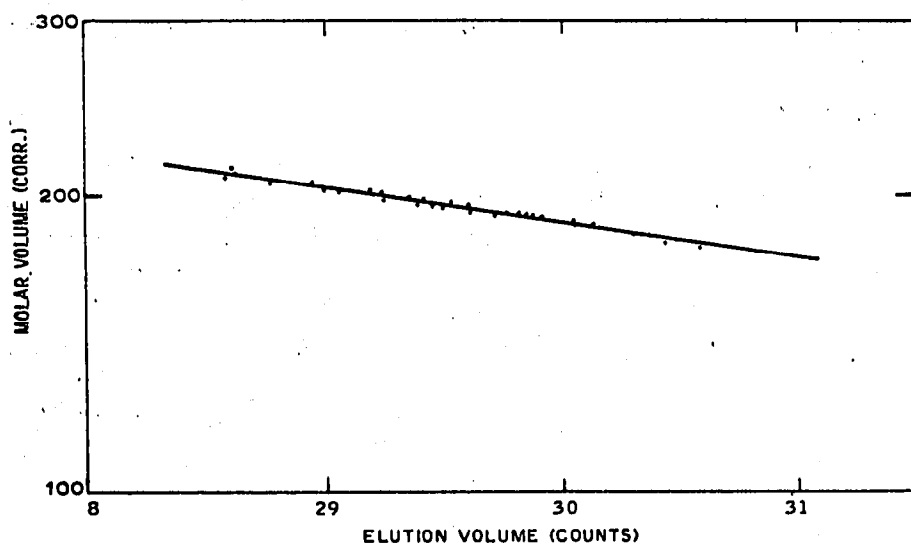


Fig. 4. Common GPC calibration curve for branched hydrocarbons.

ever, the same molecular packing factors which allow for the accurate prediction of molar volume, also permit the prediction of elution volume. The results constitute additional support for the GPC separation mechanism to be one of volume exclusion, dependent on the volume size of the solute molecule, in contrast to gas chromatography where such correlations could not be demonstrated.

#### *Boiling point correlation*

In an attempt to develop GPC for the determination of boiling point range distribution of petroleum fractions, the interdependence of elution volume, carbon number and boiling point of normal and 2-methyl-substituted alkanes was investigated<sup>12</sup>. The elution volumes for the two homologous series could be correlated with boiling points through two log-linear segments with a slope change at C<sub>12</sub>.

Fig. 5 represents a plot of boiling points against elution volume of all C<sub>8</sub>-isomers

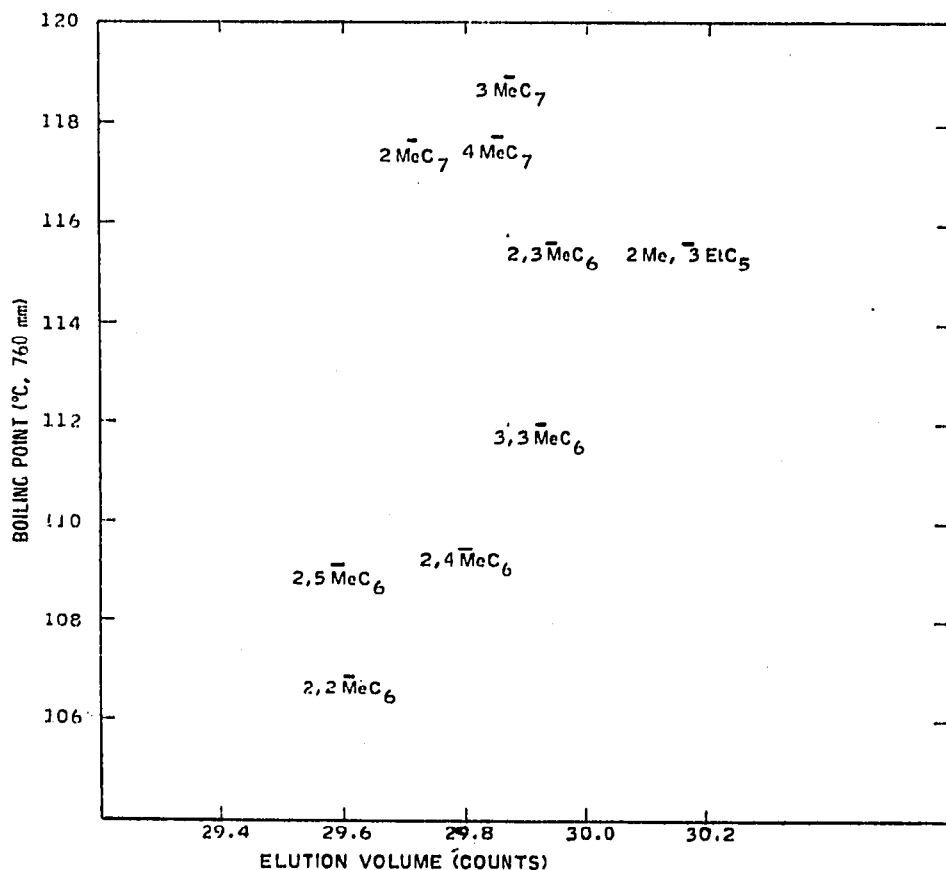


Fig. 5. Correlation of boiling point of octane isomers with GPC elution volume.

investigated. A correlation coefficient of only 0.47 was calculated. Boiling data were taken from API tables<sup>13</sup>. The absence of a boiling point correlation makes it doubtful that a simple approach to the use of GPC for the measurement of boiling point range distributions of petroleum fractions can be developed.

#### *Detector response correlation*

The common method of GPC effluent monitoring is through measurement of differential refractive index. While it is desirable for the detector response to be pro-

portional to mass of solute only, it will be affected also by changes in composition and molecular weight, particularly in the low-molecular-weight range.

The cited correlations between refractive index and structure of hydrocarbons have a direct bearing on detector response. For non-polar substances in solution, being essentially free of strong solute-solute and solute-solvent interactions, the Gladstone-Dale rule has been adequate in predicting specific refractive index increments ( $dn/dc$ ) from bulk refractive indices<sup>14</sup>. The GPC detector response is expected to be inversely proportional to molecular weight for a homologous series and proportional to  $Z_g$  for isomers. The extrapolated refractive index plots of Fig. 6 intersect at a common point,

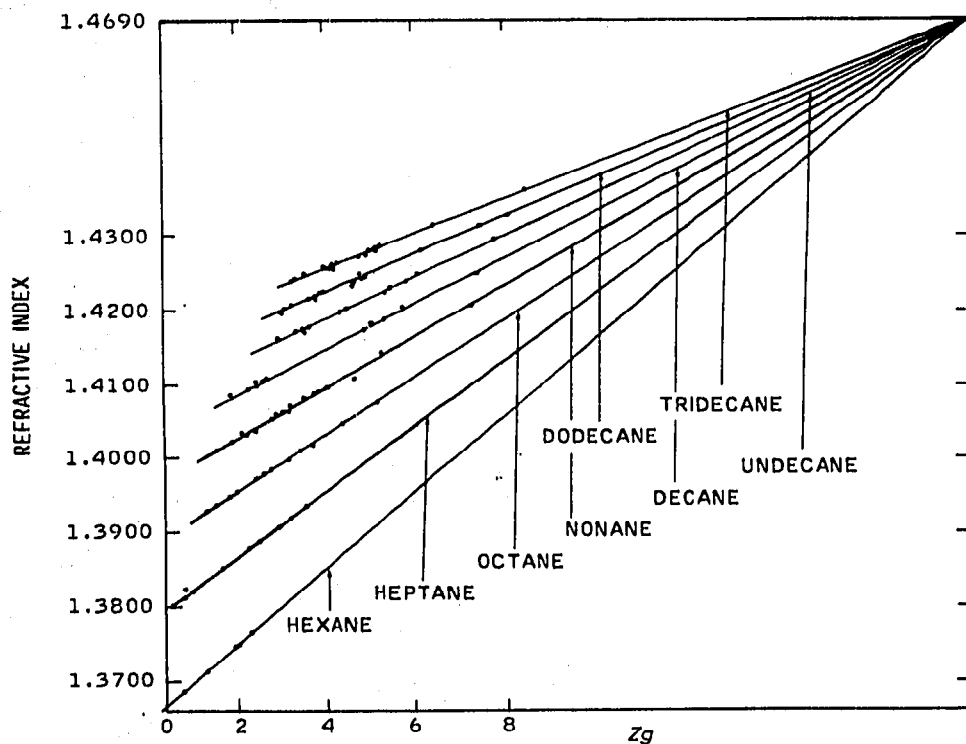


Fig. 6. Correlation of refractive index with average number of gauche conformers ( $Z_g$ ) and carbon number.

predicting that a limiting refractive index for saturated hydrocarbons be reached at a value of 1.47. At this point, refractive index would be insensitive to molecular weight and structure. The limiting  $Z_g$ -value is approximately 20.

#### CONCLUSIONS

GPC elution volumes of branched hydrocarbons do not depend on hydrocarbon molar volume alone, but reflect the separate contributions that carbon number and average number of gauche conformers make to molar volume. The systematic contributions allow one to predict elution behavior of other branched alkanes. Similar systematic correlations between boiling point and GPC elution volume do not exist. The correlation of bulk refractive index with structure and molecular weight is useful for introducing detector response corrections in connection with the chromatogram evaluation of hydrocarbon mixtures.



## REFERENCES

- 1 G. MANN, *Tetrahedron*, 23 (1967) 3375.
- 2 G. MANN, H. MÜHLSTÄDT, J. BRABAND AND E. DÖRING, *Tetrahedron*, 23 (1967) 3393.
- 3 H. BENOIT, Z. GRUBISIC, P. REMPP, D. DECKER AND J. G. ZILLIOX, *J. Chem. Phys.*, 63 (1966) 1507.
- 4 Z. GRUBISIC, P. REMPP AND H. BENOIT, *J. Polym. Sci. B*, 5 (1967) 753.
- 5 K. A. BONI, F. A. SLIEMERS AND P. B. STICKNEY, *J. Polym. Sci. A-2*, 6 (1968) 1579.
- 6 J. G. HENDRICKSON AND J. C. MOORE, *J. Polym. Sci. C* 8, (1965) 233; *ibid.*, A-1 4, (1965) 167.
- 7 J. G. HENDRICKSON, *4th Intern. Seminar Gel Permeation Chromatography*, Preprints, 1967, p. 139.
- 8 W. B. SMITH AND A. KOLLMANSBERGER, *J. Phys. Chem.*, 69 (1965) 4157.
- 9 J. CAZES AND D. R. GASKILL, *Separ. Sci.*, 2 (1967) 421.
- 10 T. EDSTROM AND B. A. PETRO, *J. Polym. Sci. C*, 21 (1968) 171.
- 11 R. E. THOMPSON, E. G. SWEENEY AND D. C. FORD, *J. Polym. Sci. A-1*, 8 (1970) 1165.
- 12 E. G. SWEENEY, R. E. THOMPSON AND D. C. FORD, *J. Chromatog. Sci.*, 8 (1970) 76.
- 13 *Selected Values of Hydrocarbons and Related Compounds*, Amer. Petrol. Inst., Project 44, Table 3A, Part 1, April 1956.
- 14 A. BELLO AND G. M. GUZMAN, *Europ. Polym. J.*, 2 (1966) 85.

*J. Chromatog.*, 55 (1971) 73-81