

GAS CHROMATOGRAPHIC DETERMINATION OF BOILING POINTS OF C₁₁-C₁₆ LINEAR ALKYL BENZENES USING PROGRAMMED TEMPERATURE OPERATION

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INTRODUCTION

The direct relationship between retention time and carbon number or boiling point in a homologous series during a programmed temperature operation has been experimentally verified by a number of authors²⁻⁶. One application of this relationship is the chromatographic simulated distillation of petroleum products. The present application utilizes this relationship for the determination of the boiling points of the positional isomers of C₁₁-C₁₆ linear alkylbenzenes. American Petroleum Institute [API] boiling point data for the 1-phenyl isomers are accurately known and have been used to establish the boiling point curve in this range. The seven homologs [C₉-C₁₅] all fell nicely on a straight line from which the other boiling points were read. Direct use of the chromatogram with proper choice of temperature axis makes the technique more rapid than plots of abstracted data.

EXPERIMENTAL

The instrument used was an F and M Model 810 gas chromatograph with flame ionization detector and a Honeywell Model 15 1 mV, one second full-scale response recorder. The instrument was modified for on-column injection as previously described⁷. This modification involves the use of a specially designed insert and requires no major modification of the instrument.

The columns used (200 ft. × 0.0625 in. O.D. × 0.02 in. I.D.) were coated from a 3% solution of the liquid phase in *n*-hexane at 60 p.s.i.g. nitrogen pressure. The tubing used was Handy and Harmon Tube Company (Norristown, Pa., U.S.A.) 316 stainless steel, 10-32 microfinish, annealed to a bright finish. After purging with nitrogen for several hours, the column was conditioned overnight at 250° with helium flowing at 6 ml per min. Prior to this work the columns had been used for several months under programmed conditions to 270° and were well conditioned for operation to this temperature.

The sample size routinely used was 0.1 μl of approximately a 10% solution of the alkylbenzenes in benzene solution. Resolution was slightly improved by using the solution instead of the neat liquid.

Blends of the various components were prepared by fortifying C₁₁-C₁₄ and

C_{14} - C_{16} alkylbenzene reaction mixtures with the 1-phenylalkanes for easier identification of the components.

The chart paper used was Graphic controls No. 9284-N. The time axis is divided into ten divisions per in. and the response axis into 120 divisions full width [11 in.]. By choosing the recorder zero as 270° and letting each division equal 1° , the boiling point range from 1-phenylnonane to 1-phenylpentadecane (282° to 366°) was made to cover full scale. Using a chart speed of 1/2 or 1 in. per minute permitted the time to be read to ± 1 -2 seconds.

Boiling points of the various isomers were obtained either directly from the boiling point curve or by calculation from the slope of the line as calculated from the boiling points and retention times for the 1-phenylalkanes.

DISCUSSION

BAUMANN, STRAUS AND JOHNSON¹ have presented boiling point data for the C_{10} - C_{16} straight chain alkylbenzenes obtained from isothermal gas chromatographic data on two columns (200 ft. \times 0.02 in. SF-96 and 200 ft. \times 0.01 in. Apiezon L). The two nonpolar stationary phases were chosen to minimize selective interactions with the phenyl group of the isomers; however, boiling points corrections of 0.7 - 4.1° were applied depending on the positional isomer. The corrected boiling points from each column were in good agreement.

The two liquid phases used in the present study were chosen mainly because of their ability to operate at the higher column temperatures employed without appreciable bleed. It was further felt that the phenyl-silicone interaction with the isomer phenyl group would be the predominant factor, outweighing slight differences caused by a positional change. This interaction should tend to be more constant and little correction should be necessary for the position on the chain.

Fig. 1 is a typical chromatogram of the C_9 - C_{16} alkylbenzene mix separated on the SE-54 capillary column programmed from 50° to 270° at 6° per min (other conditions given on the figure). Identification of components is given in Table I. The sample was an alkylation product fortified with the 1-phenyl homologs for identification. Identification of the various positional isomers was by comparison with the work of BAUMANN, STRAUS AND JOHNSON and with Perkin-Elmer gas chromatographic data sheet GC-DS-026 (Perkin-Elmer Corporation, Norwalk, Conn., U.S.A.).

Table II lists the boiling points of the alkylbenzenes as determined from chromatograms such as Fig. 1. The boiling point given is the average of two or more runs; deviation between runs averaged 0.1 - 0.3° .

Agreement of the boiling points with previous data¹ is in general quite good. Agreement for 3-phenyldodecane with the data of BAUMANN, STRAUS AND JOHNSON is good. This is significant in that 3-phenyldodecane was one of the compounds used to obtain the correction factors. The data also agrees well with the value of 318.9° for the boiling point of 7-phenyltridecane as determined by DTA. This was the second compound used by BAUMANN *et al.* for boiling point correction.

Attempts were made to use a slower program rate (4° /min) at the same flow rate. No advantage was gained in resolution and the peaks tended to exhibit more asymmetry. In addition loss of linearity for components eluting before 1-phenyldecane precluded accurate estimation of the boiling point. Faster program rates (8 - 10° /min)

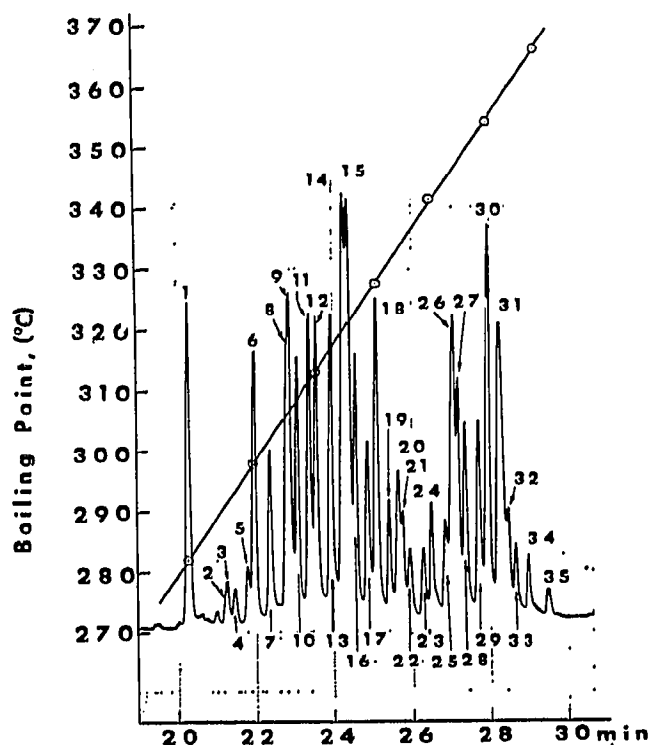


Fig. 1. Chromatogram of C_0 - C_{16} linear alkylbenzenes on SE-54 capillary column. Conditions: 50° to 270° at 6° per min. Flow: 8 ml He per min. Injection port temperature: 350° . Detector temperature: 350° . Sample size: $0.1 \mu\text{l}$ 10% solution in benzene. Electrometer range: 100 [10^{-11} A full scale]. Attenuation: $\times 8$. Hydrogen flow: 30 ml per min. Air flow: 300 ml per min. Component identification given in Table I.

TABLE I

IDENTIFICATION OF COMPONENTS IN FIG. 1

| | | | |
|----|-------------------|----|---|
| 1 | 1-Phenylnonane | 18 | 1-Phenyldodecane |
| 2 | 6-Phenylundecane | 19 | 2-Phenyltridecane |
| 3 | 5-Phenylundecane | 20 | 7-Phenyltetradecane |
| 4 | 4-Phenylundecane | | 6-Phenyltetradecane |
| 5 | 3-Phenylundecane | 21 | 5-Phenyltetradecane |
| 6 | 1-Phenyldecane | 22 | 4-Phenyltetradecane |
| 7 | 2-Phenylundecane | 23 | 3-Phenyltetradecane |
| 8 | 6-Phenyldodecane | 24 | 1-Phenyltridecane |
| 9 | 5-Phenyldodecane | 25 | 2-Phenyltetradecane |
| 10 | 4-Phenyldodecane | 26 | 8-Phenylpentadecane |
| 11 | 3-Phenyldodecane | | 7-Phenylpentadecane |
| 12 | 1-Phenylundecane | | 6-Phenylpentadecane |
| 13 | 2-Phenyldodecane | 27 | 5-Phenylpentadecane |
| 14 | 7-Phenyltridecane | 28 | 4-Phenylpentadecane |
| | 6-Phenyltridecane | 29 | 3-Phenylpentadecane |
| 15 | 5-Phenyltridecane | 30 | 1-Phenyltetradecane |
| 16 | 4-Phenyltridecane | 31 | 2-Phenylpentadecane |
| 17 | 3-Phenyltridecane | | 8-Phenylhexadecane |
| | | | 7-Phenylhexadecane + 6-phenylhexadecane |
| | | 32 | 5-Phenylhexadecane |
| | | 33 | 4-Phenylhexadecane |
| | | 34 | 3-Phenylhexadecane |
| | | 35 | 2-Phenylhexadecane |

reduced the resolution. No systematic study was made with varying flow rates. Observations in this laboratory have indicated flow rates in the range used to be about optimum for this size capillary column.

Incomplete resolution of 6- and 5-phenylundecane permits only the reporting of the same boiling point for the two isomers. A definite shoulder on the front side of the peak (presumably 6-phenylundecane) would indicate the boiling point for the 6-phenyl to be lower than given in Table II by about 0.4–0.5°.

TABLE II

BOILING POINTS OF C₁₁–C₁₆ LINEAR ALKYL BENZENES

Columns: (1) SE-52 capillary column; (2) SE-54 capillary column; (3) reference 1, Apiezon L capillary column; (4) reference 1, SF-96 capillary column.

| Compound | 1 | 2 | 3 | 4 |
|---------------------|-------|-------|-------|-------|
| 6-Phenylundecane | 291.4 | 291.6 | 288.7 | 290.2 |
| 5-Phenylundecane | 291.4 | 291.6 | 289.9 | 290.2 |
| 4-Phenylundecane | 293.8 | 293.2 | 292.0 | 291.8 |
| 3-Phenylundecane | 296.7 | 296.4 | 295.0 | 295.6 |
| 2-Phenylundecane | 301.9 | 301.8 | 301.9 | 301.6 |
| 6-Phenyldodecane | 305.2 | 305.6 | 304.0 | 304.5 |
| 5-Phenyldodecane | 305.6 | 306.2 | 304.8 | 305.1 |
| 4-Phenyldodecane | 307.6 | 308.1 | 307.3 | 307.2 |
| 3-Phenyldodecane | 310.8 | 311.2 | 310.9 | 310.7 |
| 2-Phenyldodecane | 316.4 | 316.8 | 317.2 | 316.5 |
| 7-Phenyltridecane | 319.0 | 319.6 | 318.3 | 318.6 |
| 6-Phenyltridecane | 319.0 | 320.0 | 318.3 | 318.6 |
| 5-Phenyltridecane | 319.8 | 320.7 | 319.6 | 319.6 |
| 4-Phenyltridecane | 321.2 | 322.5 | 321.8 | 321.6 |
| 3-Phenyltridecane | 325.6 | 325.3 | 325.5 | 325.0 |
| 2-Phenyltridecane | 330.5 | 331.1 | 331.2 | 330.6 |
| 7-Phenyltetradecane | 332.5 | 333.4 | 331.8 | 331.8 |
| 6-Phenyltetradecane | 332.5 | 333.4 | 332.2 | 332.3 |
| 5-Phenyltetradecane | 333.8 | 333.8 | 333.3 | 333.4 |
| 4-Phenyltetradecane | 335.8 | 336.0 | 335.3 | 335.2 |
| 3-Phenyltetradecane | 339.2 | 339.3 | 339.0 | 338.5 |
| 2-Phenyltetradecane | 344.8 | 344.4 | 344.2 | 343.7 |
| 8-Phenylpentadecane | 346.2 | 346.2 | 344.6 | 345.0 |
| 7-Phenylpentadecane | 346.2 | 346.2 | 344.6 | 345.0 |
| 6-Phenylpentadecane | 346.6 | 346.2 | 345.2 | 345.6 |
| 5-Phenylpentadecane | 347.8 | 347.2 | 346.3 | 346.7 |
| 4-Phenylpentadecane | 349.7 | 349.2 | 348.4 | 348.6 |
| 3-Phenylpentadecane | 352.9 | 352.6 | 351.6 | 351.7 |
| 2-Phenylpentadecane | 357.2 | 358.0 | 357.0 | 356.8 |
| 8-Phenylhexadecane | 357.8 | 357.4 | | |
| 7-Phenylhexadecane | 357.8 | 357.4 | | |
| 6-Phenylhexadecane | 359.3 | 358.8 | | |
| 5-Phenylhexadecane | 360.5 | 360.0 | | |
| 4-Phenylhexadecane | 362.4 | 361.4 | | |
| 3-Phenylhexadecane | 365.2 | 364.7 | | |
| 2-Phenylhexadecane | 370.3 | 369.0 | | |

It should be noted that the chromatogram shown in Fig. 1 is illustrative of the degree of resolution obtained in this work. The boiling points given in Table II for some components shown as being co-eluted in the figure were obtained from chromatograms of narrower range fractions. For example the boiling point of 2-phenylpentadecane was obtained from a chromatogram in which resolution of this component from the 8-, 7-, and 6-phenylhexadecanes was better than indicated in the figure. Some doubt does exist, however, as to the correct assignment of peaks in this region. The data point for the boiling point of 1-phenylpentadecane (not shown in the figure) was obtained by comparison with other chromatograms.

While used in the present work for the estimation of boiling points, use of the direct relationship between retention time and boiling point with data plotted directly on the chromatogram is a valuable general technique for identification of components for which boiling point data is known. Use of the technique in the C_8 - C_{10} aromatic region with the capillary columns used in this work and coated with other nonpolar or slightly polar liquid phases has permitted the estimation of the boiling point of unknown components to within 0.2° . Since boiling point data is available for most of the aromatic compounds in this region, identification on the basis of boiling point is a valuable aid to other auxiliary techniques, such as rapid-scan mass spectrometric analysis. The combination of a (rapid-scan) mass spectrogram and the boiling point can, in many cases, give a unique identification of a component which is not available for direct comparison.

CONCLUSIONS

The accuracy of the boiling points given in Table I is difficult to judge. Agreement with the data of BAUMANN, STRAUS AND JOHNSON is reasonable, especially for most of the 2- and 3-phenyl isomers. Boiling points for the 7-, 6-, and 5-phenyl isomers tend to be somewhat higher, while data for the 4-, 3-, and 2-phenyl isomers is generally in agreement by at least 1.0° . The accuracy is dependent on the (assumed) linearity of retention time with boiling point and the (assumed) negligible effect of phenyl position on partition coefficient. The boiling points are believed to be accurate to less than 1° .

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SUMMARY

Boiling points of the positional isomers of C_{11} - C_{16} linear alkylbenzenes have been determined on two capillary columns with programmed temperature operation. Excellent linearity of retention time *versus* boiling point of the 1-phenylalkanes [C_9 - C_{15}] was used to establish the boiling point curve. The boiling points of the various isomers were then read directly off this curve, eliminating lengthy tabulation of data for semi-log plots necessary for isothermal operation. No correction factors were applied for the positional isomers.

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