NOTE ON THE PROBABLE PRESENCE OF 2, 2-DIMETHYLPENTANE IN A MIDCONTINENT PETROLEUM [1]

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ABSTRACT

This paper presents evidence which indicates that 2, 2-dimethylpentane is present in small amount (not more than a few hundredths of 1 per cent) in a midcontinent petroleum. The evidence consists in the approximate agreement of the measured properties of a petroleum fraction containing 46 mole per cent of cyclohexane with those computed on the assumption that the remaining 54 per cent is 2, 2-dimethylpentane.

The properties compared were initial freezing point, boiling point, refractive index, molecular weight and eutectic temperature. The evidence thus obtained was confirmed by comparing the infra-red absorption spectrum of the petroleum fraction with that of a synthetic mixture having the assumed composition.

CONTENT

I. INTRODUCTION

From a Caucasian petroleum, Markownikoff (1) [3] obtained a fraction boiling between 78.5° and 79° C. From the boiling range and the specific gravity of this fraction, as well as from its unusual stability toward strong nitric acid, he concluded that 2,2-dimethylpentane was probably present in the Caucasian petroleum. With the exception of Markownikoff, it seems that no one has reported any indication of the presence of 2,2-dimethylpentane in any petroleum.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The present investigation deals with the same fractions of an Oklahoma petroleum which were used for the isolation and determination of cyclohexane (2).

It was found that a large cut (5.5 kg) boiling between 80° and 80.5° C. consisted of about 94 mole per cent of cyclohexane and had a refractive index of 1.422 which is 0.003 unit lower than that of pure cyclohexane. It was therefore apparent that some compound

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[3] Figures in parenthesis here and elsewhere in the text indicate references given in the bibliography at the end of this paper.

or compounds with lower refractive index than that of cyclohexane must also be present in this fraction. The object of the present investigation was to concentrate this unknown constituent for possible identification.

While working on the isolation of cyclohexane, it was noted that if the cut boiling between 80° and 80.5° C. was subjected to fractionation by equilibrium melting, fractions of rapidly decreasing refractive indices were obtained. Thus by a single fractionation the following changes in the physical constants were obtained:

	Stage I Stage II
n_D^{20} changed from	1.422 to 1.417
Freezing point changed from	−12° to −28° C.
Boiling point changed from	80.4° to 80.0° C.
Molecular weight changed from	85.1 to 86.1

In view of this apparently efficient separation it was decided to subject the material to systematic equilibrium melting. The progress of the fractionation is shown by the chart in Figure 1. The large circle at the upper left corner (R. I. 1.416) represents the original fraction (obtained by distillation) which had the boiling range 79° to 80° C. The other nine large circles at the top represent fractions which were obtained by subjecting the 80.0° to 80.5° C. cut to equilibrium melting. (This fractionation is described in the cyclohexane paper (2).) The numbers inside the large circles indicate the refractive indices and the initial freezing points of the fractions. As indicated by the solid lines, the large fractions were separated by equilibrium melting into a number of smaller fractions, indicated by the smaller circles. The refractive indices of these fractions are given by the numbers inside the circles. The fractions having similar refractive indices were then mixed for further fractionation. This is indicated by the broken lines in Figure 1. As shown in the chart, the molecular weight was determined for some of the fractions.

As a result of the fractionation shown in Figure 1, the material was separated into comparatively large fractions consisting mainly of cyclohexane (fractions with high refractive indices) and into small quantities of material with low refractive index and low freezing point. Fractionation of this material, which contained the unknown constituent, was continued until its refractive index had been brought down to 1.392 and its freezing point had reached −124.6° C. (Stage III.) At this point, however, the available quantities of this material were too small to attempt further purification.

The time-temperature cooling curve of the final fraction is shown in Figure 2. Table 1 shows some of the physical constants of synthetic 2, 2-dimethylpentane, of cyclohexane, and of the petroleum fractions during three stages of the fractionation. Stage I represents the large cut boiling between 80° and 80.5° C. The material in Stage II was obtained by a single fractionation of the mixture in Stage I by equilibrium melting. (See p. 54 and upper left of fig. 1.) Stage III represents the fraction which was obtained as a final result of the systematic equilibrium melting. (See bottom of fig. 1.)

TABLE 1.—*Some physical constants of 2, 2-dimethylpentane, of cyclohexane, and of the petroleum fractions during three stages of the fractionation*

	Cyclohexane (C_6H_{12}) synthetic [a]	The petroleum fractions			2, 2-dimethylpentane (C_7H_{16}) synthetic [b]
		Stage I	Stage II	Stage III	
$n\frac{20}{D}$	1.426	1.422	1.417	1.392	1.382
Molecular weight	84.09	[c] 85.1	[c] 86.1	[c] 93.7	100.12
Normal boiling point in ° C	80.8	80.4	80.0	79.5	78.9
Freezing point in ° C	6.4	−12	−28	−124.6	−125.6

[a] J. Timmermans, J. chim. phys., vol. 23, p. 760, 1926.
[b] G. Edgar and G. Calingaert, J. Am. Chem. Soc., vol. 51, p. 1544, 1929.
[c] For method, see M. M. Hicks-Bruun, B. S. Jour. Research, vol. 5, pp. 575–583, 1930.

As the fractionation proceeded a definite increase was noted in the molecular weight. Thus, while the molecular weight for Stage I was 85.1, the material in Stages II and III was found to have molecular weights of 86.1 and 93.7, respectively. This is unmistakable evidence of the presence of a constituent having a higher molecular weight than that (84.09) of cyclohexane.

The material in Stage III had a distillation range of about 0.5° C. It did not react with bromine or iodine and it was insoluble in water. Furthermore this fraction exhibited an unusual stability when heated with fuming nitric or with chlorosulphonic acid.

By correlating the values of the molecular weight (93.7), the refractive index and the boiling point of this fraction with the corresponding constants of known hydrocarbons, it was concluded that a heptane was probably present in the cyclohexane fraction.

It should be further noted that the boiling point of the material in Stage I (which contained 94 mole per cent of cyclohexane) was 80.4° C. as compared with 80.8° C. for pure cyclohexane. As a result of further fractionation by equilibrium melting fractions of still lower boiling points (80.0° C. in Stage II and 79.5° C. in Stage III) were obtained. This fact indicates clearly that the presumed heptane is one with a boiling point below that of cyclohexane or that the mixture is azeotropic with a boiling point minimum. The only heptane with a boiling point below 80.8° is 2,2-dimethylpentane.

The above-mentioned great stability of the material in Stage III against chemical reagents is in accordance with the structure of 2,2-dimethylpentane, because of all the isomeric heptanes, only the following three do not possess a reactive tertiary carbon atom: 2,2-dimethylpentane (boiling point 78.9° C.); 3,3-dimethylpentane (boiling point 86° C.); and *n*-heptane (boiling point 98.4° C.).

III. ANALYSIS OF THE FINAL FRACTION

For the purpose of determining the approximate composition of the material (Stage III, Table 1) having the lowest refractive index (1.392), the following procedure was used. The freezing point of cyclohexane was determined with a Beckmann thermometer. A solution of known concentration of the material (Stage III) in the cyclohexane was then made up, after which the lowering of the freez-

ing point was determined. It is evident that the cyclohexane present in the material (Stage III) will have no effect upon the freezing point, and that the total lowering will be caused by the other con-

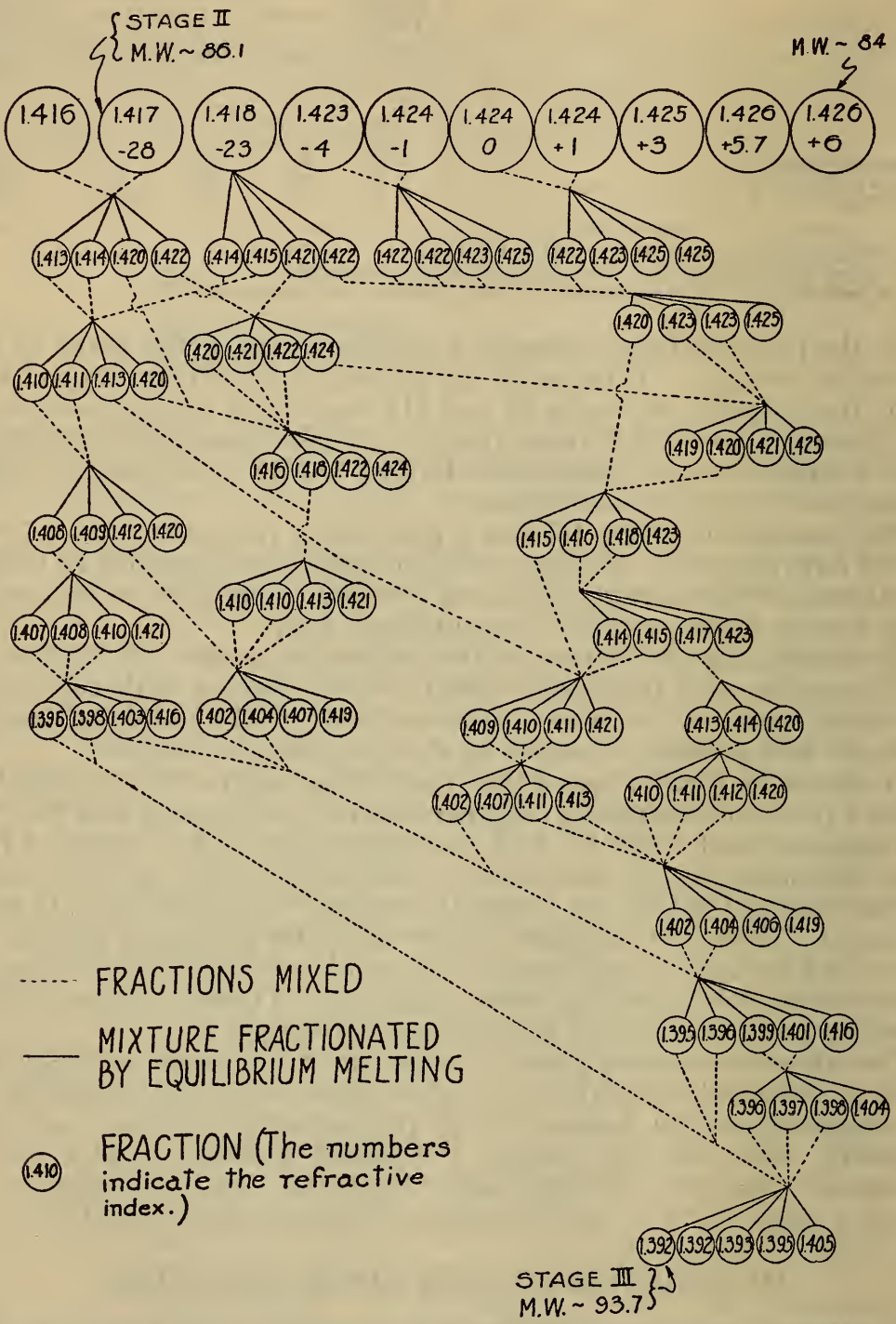

FIGURE 1.—*Chart showing the fractionation by means of equilibrium melting*

stituents in this material. From the lowering thus obtained the mole percentage of cyclohexane for the material in Stage III could be calculated. However, the two most recent values reported in the literature for the heat of fusion (L_{f_0}) of cyclohexane differ by more

than 20 per cent. Hence calculations were made using each value, with these results:

$L_{fo} = 5.87$ cal./g (3).
45.9 mole per cent of cyclohexane and
54.1 mole per cent of other constituents.
$L_{fo} = 7.4$ cal./g (4).
30.8 mole per cent of cyclohexane and
69.2 mole per cent of other constituents.

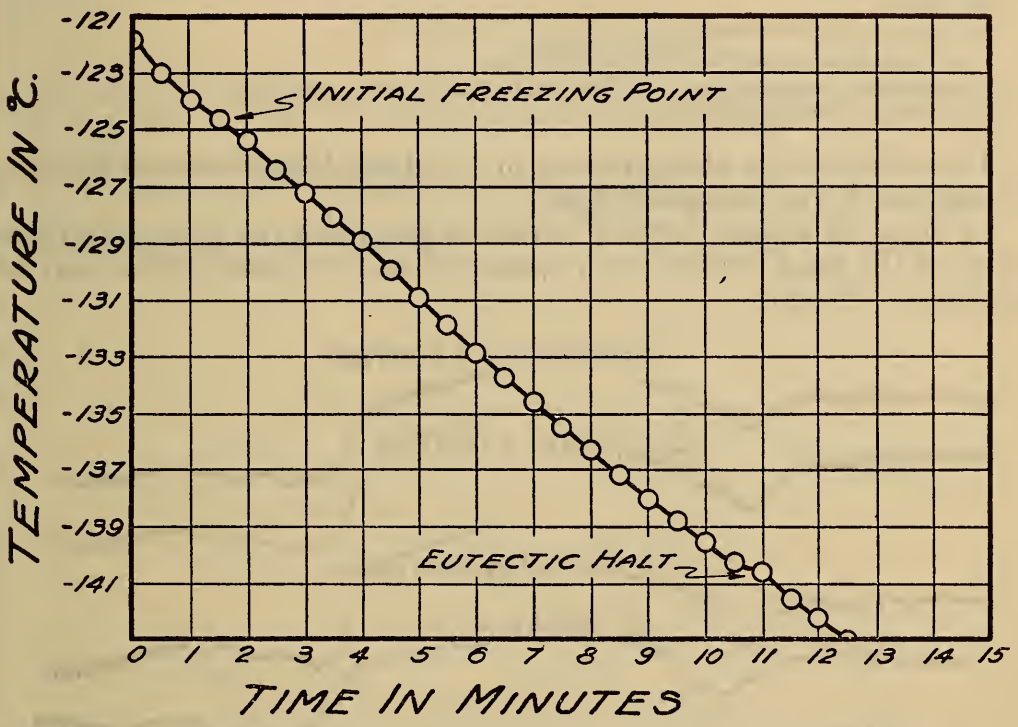

FIGURE 2.—*Time-temperature cooling curve of the final fraction. (Stage III)*

IV. CORRELATION OF THE PROPERTIES OF THE FINAL FRACTION WITH ITS COMPOSITION

The amount of the final fraction (Stage III) was so small that further fractionation for the purpose of isolating a pure sample of the presumed heptane was impossible. Under these circumstances the best that can be done is to compare the measured properties of the final fraction with those of a mixture consisting of 45.9 moles of cyclohexane and 54.1 moles of 2,2-dimethylpentane. This comparison is shown in Table 2. The calculated values are based on the assumption that the mixture is an ideal solution.

It will be observed that the agreement is good except in the case of the refractive index, where the observed value is low by 0.008 unit, which might be caused by the presence of a small amount of a third constituent, such as normal hexane, for example.

TABLE 2.—*Observed and calculated properties of the final fraction*

Property=	F. P.[a]	B. P.[a]	Molecular weight	n_D^{20}	Eutectic halt
	°C.	°C.			°C.
Observed values	−124.6	79.5	93.7	1.392	[b]−140.2
Values calculated from L_{f_0}=5.87 cal./g[c]	−124.6	79.8	92.8	[d]1.399	[e]−138.2
L_{f_0}=7.4 cal./g[f]	−136.8	----------	95.1	1.394	[e]−136.0

[a] Initial.
[b] See Figure 2.
[c] See reference (3) in bibliography.
[d] A synthetic mixture was found to have n_D^{20}=1.400.
[e] For method see Washburn and Read, Proc. Nat. Acad., vol. 1, p. 191, 1915.
[f] See reference (4) in bibliography.

The evidence for the presence of 2,2-dimethylpentane is therefore strong but by no means decisive.

In order to obtain further evidence the infra-red absorption spectrum of the final fraction was measured and compared with that of a synthetic mixture.

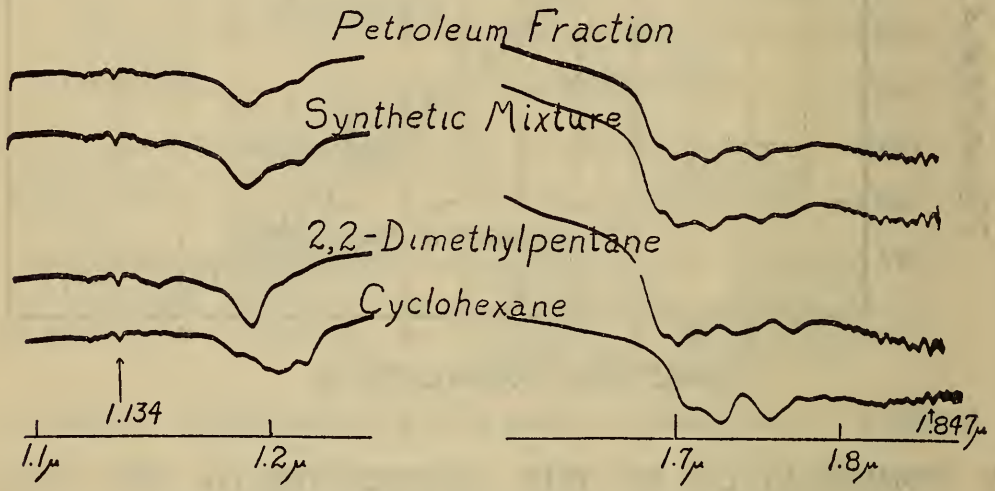

FIGURE 3.—*The infra-red absorption spectra of the final petroleum fraction (Stage III), the synthetic mixture, the 2,2-dimethylpentane, and the cyclohexane*

Measured by U. Liddel, of the Fixed Nitrogen Research Laboratory of the Department of Agriculture.

Through the courtesy of G. Edgar and G. Calingaert, of the Ethyl Gasoline Corporation, a small sample of synthetic 2,2-dimethylpentane was obtained. This sample was mixed with pure cyclohexane (and a small amount of *n*-hexane) so as to yield a mixture of approximately the same composition as that calculated for the material in Stage III. The spectra of the two mixtures as well as those of the pure samples of cyclohexane and of 2,2-dimethylpentane were then measured by U. Liddel, of the Fixed Nitrogen Research Laboratory of the United States Department of Agriculture, and are shown in Figure 3. The two upper curves reveal a striking resemblance between the synthetic mixture and the final fraction (Stage III), which was presumably of the same composition.

The characteristic minimum at about 1.19μ is clearly evident in the spectrum of the petroleum fraction. This evidence when taken together with that shown in Table 2 renders it highly probable that 2,2-dimethylpentane is a major constituent of the petroleum fraction

(Stage III). Based upon the crude oil the amount present can not, however, exceed a few hundredths of 1 per cent. With larger amounts of material to work with, there should be no difficulty in isolating the pure hydrocarbon.

V. ACKNOWLEDGMENT

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VI. BIBLIOGRAPHY

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