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RELATIONSHIPS BETWEEN PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION OF LUBRICATING OIL FRACTIONS[1]

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ABSTRACT

A correlation of the physical properties of a series of petroleum fractions in the lubricating-oil region with each other and with the physical properties of synthetic hydrocarbons of high molecular weight has been made. The petroleum fractions had been extensively separated by distillation and extraction and their empirical formulas determined. The following properties were compared: densities, specific refractions, optical activities, specific dispersions, viscosities, viscosity indices, aniline points, and boiling points.

It appears that the least soluble portion of the oil, that is, the material corresponding to the most highly refined product obtained by any good solvent extraction process, consists substantially of naphthenes (cycloparaffins) containing from one to about three rings to the molecule, together with the necessary alkyl radicals. The somewhat more soluble portion consists of naphthenes with more rings, together with some unsaturated hydrocarbons and possibly some aromatic hydrocarbons. There is no evidence whatever for the existence of iso or branched-chain paraffins.

Because of the similar solubility relations, it is possible that in the extraction processes as used at the present time one-ring aromatic hydrocarbons are being discarded to waste along with the undesirable naphthenes containing about six rings to the molecule. This is a point well worth investigating, since these one-ring aromatic hydrocarbons may be a valuable constituent for good lubricating oil.

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[1] Financial assistance for this work has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum. This paper was originally presented before the American Chemical Society at the Pittsburgh meeting in September 1936.

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I. INTRODUCTION

The literature dealing with the constitution of the lubricant fraction of petroleum has recently been reviewed by Mikeska [1] [3] and Rossini [2]. An examination of these and other articles shows a considerable divergence of opinion as to what types of hydrocarbons are present and what relationships exist between chemical constitution and physical properties. The feeling of doubt which exists regarding the chemical nature of the high-boiling fractions of petroleum is exemplified by the following quotation from a recent paper by Lane and Garton [3]: "From the standpoint of pure chemistry the use of 'paraffin', 'naphthene', and similar terms as applied to the heavy ends of crude petroleum is still less justified. There are virtually no published data on the higher boiling fractions of crude oil which would indicate in a reliable manner the chemical nature of the compounds present."

One of the factors which has materially retarded knowledge in this field has been the lack of information concerning the physical properties of synthetic hydrocarbons of high molecular weight. Recently a large number of hydrocarbons of high molecular weight have been synthesized, principally by Mikeska [1], and many of their physical properties determined, so that a direct comparison of their properties with those of petroleum fractions is now possible.

In this laboratory there have recently been prepared from a midcontinent crude petroleum by extensive distillation and extraction a series of lubricating-oil fractions, which are perhaps more homogeneous with respect to type of molecule and molecular weight than any fractions hitherto obtained from lubricating oil. In the expectation of clearing up some of the existing differences of opinion, and in extending the knowledge of the chemical constitution of the lubricant fraction, this paper presents a correlation and comparison of the physical properties of these fractions with each other, and with those of synthetic hydrocarbons of high molecular weight.

II. ORIGIN AND HISTORY OF THE PETROLEUM FRACTIONS

The origin of the lubricating-oil stock was well no. 6 of the South Ponca Field, Kay County, Okla. Before receipt at this Bureau, the portion of the crude petroleum containing the lubricating oil was fractionally distilled in "vacuo" by the Sun Oil Co. at Philadelphia. Its treatment after receipt at this Bureau is described in detail elsewhere [4, 5] and is illustrated diagrammatically in figure 1. Briefly, this treatment consisted in the preparation of a "water-white" oil by extraction with sulphur dioxide, by removal of wax, and by filtration through silica gel. This water-white oil was then fractionally distilled until substantially constant-boiling fractions were obtained. Charges with narrow boiling range were then extracted with acetone in 14-meter columns, each charge being separated into about 25 to 30 fractions. A number of fractions from six of the charges (designated as series *A*, *B*, *C*, etc., in fig. 1) were selected as key fractions and their empirical formulas, together with a large number of physical proper-

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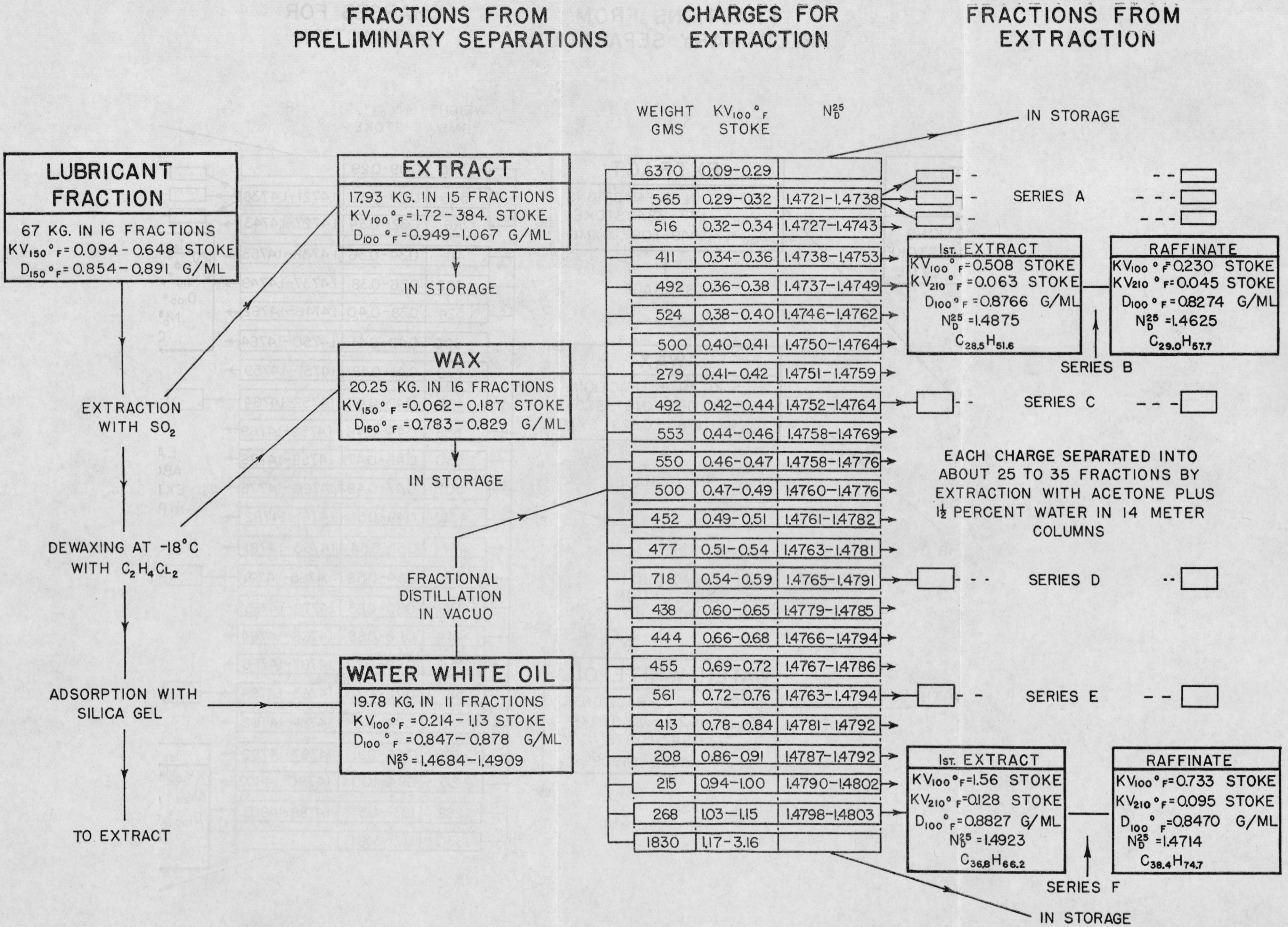
[3] The figures given in brackets here and elsewhere in the text correspond to the numbered references at the end of this paper.



WEIGHT GMS	$KV_{100°F}$ STOKE	N_D^{25}
6370	0.09-0.29	
565	0.29-0.32	1.4721-1.4738
516	0.32-0.34	1.4727-1.4743
411	0.34-0.36	1.4738-1.4753
492	0.36-0.38	1.4737-1.4749
524	0.38-0.40	1.4746-1.4762
500	0.40-0.41	1.4750-1.4764
279	0.41-0.42	1.4751-1.4759
492	0.42-0.44	1.4752-1.4764
553	0.44-0.46	1.4758-1.4769
550	0.46-0.47	1.4758-1.4776
500	0.47-0.49	1.4760-1.4776
452	0.49-0.51	1.4761-1.4782
477	0.51-0.54	1.4763-1.4781
718	0.54-0.59	1.4765-1.4791
438	0.60-0.65	1.4779-1.4785
444	0.66-0.68	1.4766-1.4794
455	0.69-0.72	1.4767-1.4786
561	0.72-0.76	1.4763-1.4794
413	0.78-0.84	1.4781-1.4792
208	0.86-0.91	1.4787-1.4792
215	0.94-1.00	1.4790-1.4802
268	1.03-1.15	1.4798-1.4803
1830	1.17-3.16	

FIGURE 1.—*Chart showing treatment and disposition of lubricating oil fractions.*

ties, determined. These data, which have been published in tables 2 and 3 of the preceding paper [5], are the basis for the correlation contained in this paper.

III. SYNTHETIC HYDROCARBONS

The physical properties of the synthetic hydrocarbons used in this comparison are principally those reported by Mikeska [1]. In addition, values for 16-butylhentriacontane from Suida and Planckh [6], dimethyl-9,12-di-*n*-hexyl-9,10-octadecane from Lerer [7], 1,1-dicyclohexylhexadecane and 1-cyclohexyl-2-hexahydrobenzylheptadecane from Landa and Cech [8] have been used in the charts of specific refraction and density. Also used in the density chart is the value for 1-phenyl-2-benzylheptadecane from Landa and Cech [8]. In addition to Mikeska's [1] values, the viscosity and viscosity-index charts contain values for 1,1-dicyclohexylhexadecane and 1-cyclohexyl-2-hexahydrobenzylheptadecane. The aniline-point chart contains values determined in this laboratory for two normal paraffins. The *n*-nonacosane was prepared from apple cuticle by K. S. Markley, Bureau of Plant Industry, U. S. Department of Agriculture. The *n*-dotriacontane was a synthetic sample prepared by Y. Delcourt [9] and further purified by distillation in this laboratory.

IV. PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

In his investigations of the lubricant portion of petroleum, Mabery [10] obtained fractions with empirical formulas ranging from C_nH_{2n} to C_nH_{2n-30}. He tested his fractions for unsaturation, and, finding none, attributed the deficiency in hydrogen from the formula C_nH_{2n+2} to the presence of ring compounds. This deficiency of hydrogen in well refined oils of the Pennsylvania type is usually attributed to the presence of naphthene rings rather than of aromatic rings. However, it is known to be extremely difficult to remove aromatic hydrocarbons completely from the lubricant fraction, and the term "more naphthenic" as frequently employed signifies nothing more than an increasing deficiency of hydrogen in the formula $C_nH_{2n\pm x}$. Yet, in attempting to relate the chemical constitution and the physical properties, it is extremely important to know how much of this deficiency is attributable to naphthene rings and how much to aromatic rings. For example, as shown by the work of Mikeska [1], an aromatic with one ring and a long paraffin side chain may be expected to have a much lower viscosity and a lower temperature coefficient of viscosity (higher viscosity index) than a four-ring naphthene with the same number of carbon atoms. Yet both these compounds are represented by the same empirical formula, C_nH_{2n-6}.

In the following attempt to correlate physical properties and constitution, it was consequently of importance to decide how much of the change in empirical formula was due to a change in aromatic concentration or unsaturation, and how much to a separation into fractions containing, respectively, more or fewer naphthene rings.

Several methods which utilize such physical properties as molecular volumes (Davis and McAllister [11]), specific refractions, specific dispersions, and aniline points (Vlugter, Waterman, and Van Westen

[12]) have been used by other investigators to detect the presence of aromatics, or to determine the number of naphthenic rings in petroleum fractions. But these methods usually involved a considerable extrapolation from the properties of synthetic hydrocarbons of low molecular weight to those of high molecular weight, and it was difficult to say how reliable they were. Now, however, it is possible to check these methods with synthetic hydrocarbons of high molecular weight and arrive at a reliable picture as to the composition of the fractions under investigation.

1. DENSITIES

In figure 2 is shown a plot of the densities of a number of synthetic hydrocarbons of diverse types with respect to the number of carbon atoms they contain. Also represented by circles in the same figure are the densities of the key fractions from petroleum. The figures within these circles denote the value for x in the formula C_nH_{2n+x}. The key fractions resulting from the extraction of each charge are connected with arrows, which denote the order of their extraction. An examination of figure 2 shows that monocyclic aromatics have lower densities than bicyclic naphthenes, although the value for x in the formula C_nH_{2n+x} is -6 for monocyclic aromatics and -2 for bicyclic naphthenes. This suggests that a consideration of the values for x in conjunction with the densities may be used to determine whether an oil is composed of aromatics or naphthenes. It is evident that the densities of the less soluble key fractions are, for given values of x, in fair agreement with those of the corresponding cyclohexane derivatives, but are much too high to be accounted for on the supposition that they are composed of monocyclic aromatics, or their mixtures with isoparaffins or naphthenes. For the more soluble fractions the densities are also higher for given values of x than those of the corresponding aromatics, which suggests that they also contain naphthenes. However, the absence of synthetic naphthenes with corresponding values of x, makes a direct comparison impossible, and the fact that in some cases the density is not so markedly higher than that of the corresponding aromatics suggests that they may also contain some aromatic or unsaturated hydrocarbons. This is borne out by a consideration of their other properties.

2. SPECIFIC REFRACTIONS

An important method for detecting the presence of aromatics or unsaturated hydrocarbons in petroleum fractions, in which use is made of the specific refraction, has been employed by Vlugter, Waterman, and Van Westen [12]. These authors point out that if the Lorentz-Lorenz specific refraction, $\frac{n_D^2-1}{n_D^2+2}\cdot\frac{1}{d}$, is considered, aromatics and isoparaffins have high specific refractions, while for naphthenes the specific refraction is lower and decreases as the number of rings in the naphthene is increased. Vlugter, Waterman, and Van Westen in this work have computed theoretical values of the specific refraction for paraffins and naphthenes of high molecular weight from Eisenlohr's values for the atomic refractions of carbon (2.418) and hydrogen (1.100). This method has, however, been criticized by Griffith and Hollings [13] who state, "We do not feel that agreement between observed and calculated figures for the very few known hydrocarbons cited is sufficiently good to justify the extrapolation of the curves to include mixtures of widely different molecular weight. The fact that aromatic hydrocarbons are known not to give experimental results in agreement with those calculated is also significant."

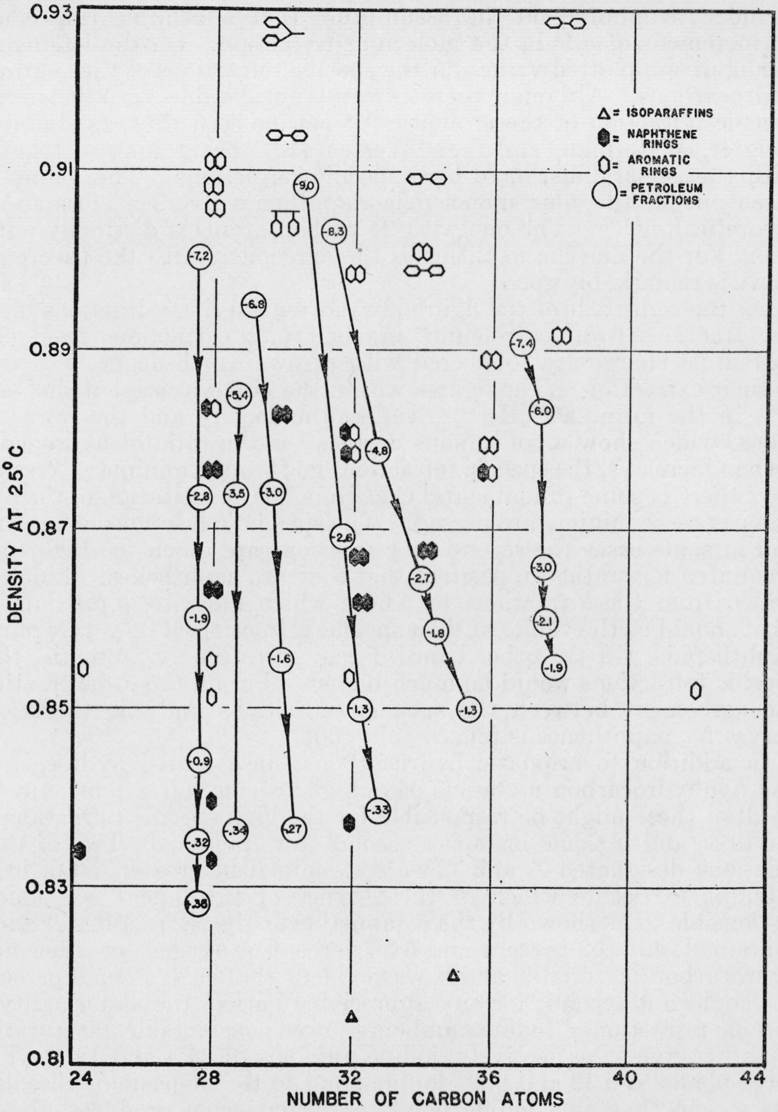


FIGURE 2.—*Densities of synthetic hydrocarbons and petroleum fractions.*

It is now possible to answer this criticism by calculating the specific refraction of a number of synthetic hydrocarbons in the region in which we are interested. This shows that Vlugter, Waterman, and Van Westen's curves for naphthenes represent the facts remarkably well, and by the use of the method one can determine which of the fractions from petroleum are free from aromatics and unsaturated hydrocarbons.

In figure 3 are shown theoretical curves similar to those of Vlugter, Waterman, and Van Westen giving the variation in specific refraction with the number of carbon atoms for paraffins and mono-, di-, and tricyclic naphthenes. In addition, a curve for monocyclic aromatics is included, computed on the assumption that a benzene ring causes an increment of 5.1[4] in the molecular refraction. On the left half of the figure are plotted values for the specific refractions of the synthetic hydrocarbons. Although there is very considerable variation in the specific refraction of the aromatics, it can be seen that, as stated by Vlugter, Waterman, and Van Westen [12] the aromatics, together with the isoparaffins, have high specific refractions. The values for three out of the four monocyclic naphthenes average close to the theoretical curve. The one with 24 carbon atoms is distinctly out of line. For the dicyclic naphthenes the agreement with the theoretical curve is remarkably good.

On the right half of the figure are plotted specific refractions of the key fractions from petroleum. As before, the fractions from each individual charge are connected with arrows which denote the order of their extraction. The figures within the circles represent the value of x in the formula C_nH_{2n+x}. Unlike the density and the refractive index, which show a continuous decrease as the ratio of hydrogen to carbon increases, the specific refractions go through minima. Presumably there is some fundamental change in the constitution of the fractions as these minima are passed. The specific refractions of the first, and in some cases the second, key fractions are much too high to be accounted for on the supposition that they are naphthenes. Lines are drawn from these fractions to points which indicate approximately what should be the values of their specific refractions if they were purely naphthenic. On the other hand, if they were purely aromatic, their specific refractions would be much higher. For all the other fractions the agreement between the specific refractions and the theoretical curves for naphthenes is remarkably good.

In addition to aromatic hydrocarbons, unsaturated hydrocarbons and nonhydrocarbon materials have high specific refractions, and one or all of these might be responsible for the high specific refractions of the first, and in some instances second, key fractions. Two of these fractions designated *A* and *C* were examined in greater detail in an attempt to decide which of these types of substances was chiefly responsible. As shown by the combustion analysis, fractions *A* and *C* contained only 0.2 percent and 0.36 percent of oxygen (or other nonhydrocarbon materials), and it was evident that such a small percentage could not account for any appreciable part of the abnormality in specific refraction. Iodine numbers showed considerable unsaturation *A* and *C* giving, respectively, iodine numbers of 21.4 and 18.1, which corresponds to 0.32 and 0.28 double bond to the molecule. Eisenlohr has shown that one double bond to the molecule produces (on the average) an increment in molecular refraction of 1.707, so that the presence of 0.32 and 0.28 double bond to the molecule would cause increments of 0.548 and 0.487 in molecular refractions, which correspond for fractions *A* and *C* to increments of 0.00154 and 0.00121 in the

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[4] This value was arrived at from a consideration of the molecular refraction of benzene, toluene, *o*-, *m*-, and *p*-xylene, and the three trimethylbenzenes.

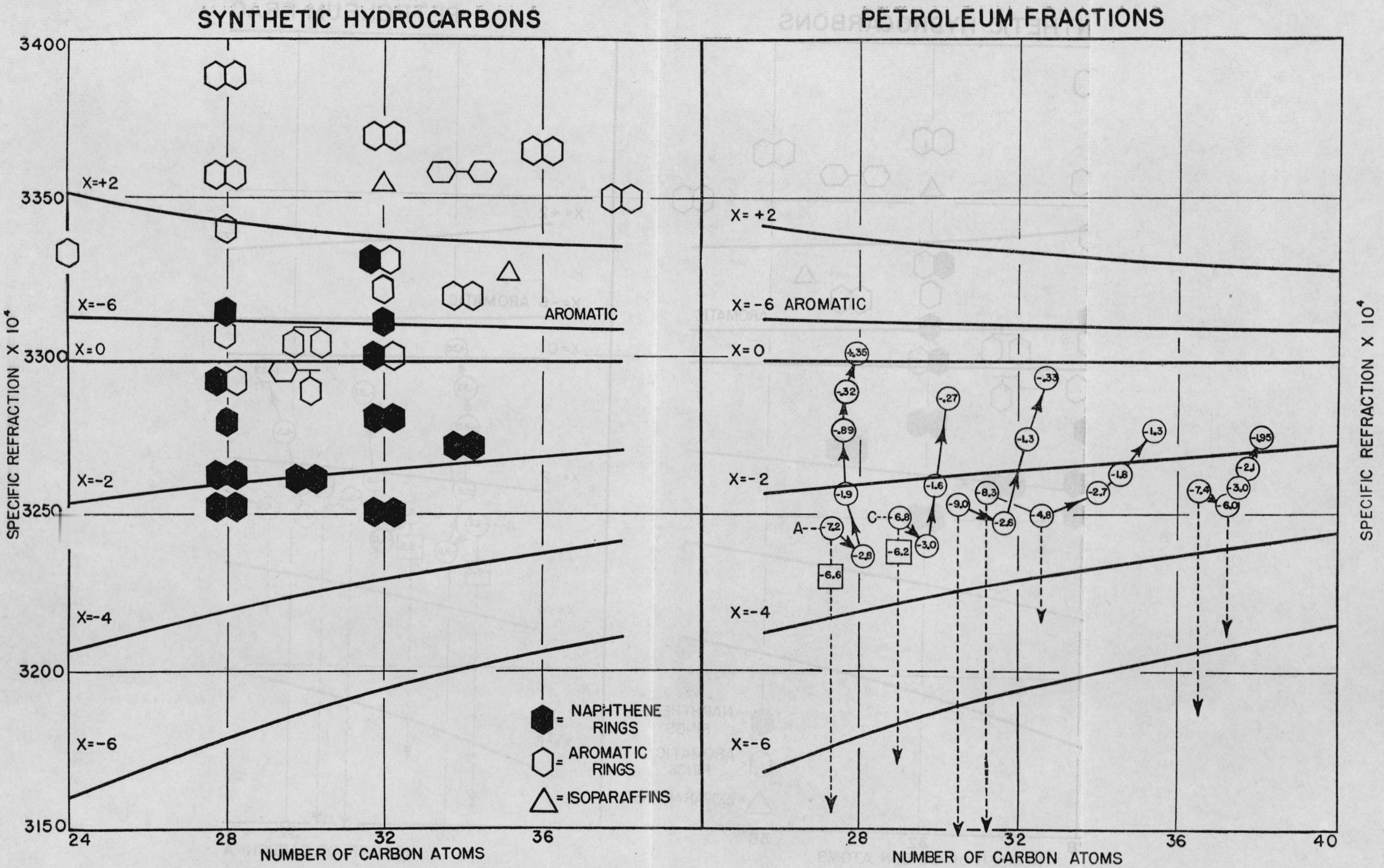

FIGURE 3.—*Specific refractions of synthetic hydrocarbons and petroleum fractions.*

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specific refraction. By subtracting these values from the specific refractions of *A* and *C*, one should obtain the specific refractions of *A* and *C* if they had contained no unsaturated material. The positions of *A* and *C* corrected in this manner are designated in figure 3 by squares, the figures within the squares indicating the x values for these fractions if they had contained no unsaturated material. It is evident that even with this correction for unsaturation the fractions have markedly higher specific refractions than the corresponding naphthenes, and it seems highly probable that they contain considerable aromatic material.

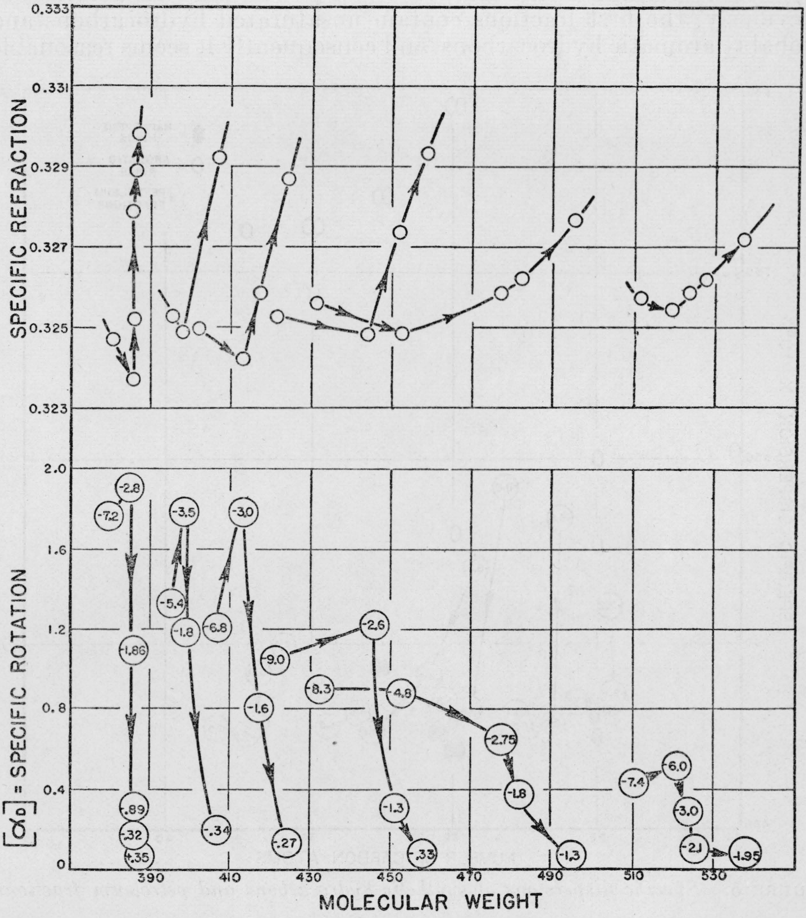

FIGURE 4.—*Parallelism between specific refractions and specific rotations of petroleum fractions.*

3. OPTICAL ACTIVITIES

The optical activity of petroleum fractions is of importance since its study may shed considerable light not only on the constitution of petroleum but also on its origin. In figure 4 are shown plots of the specific rotation and specific refraction of the key fractions with respect to molecular weight. It is evident that the optical activities decrease with increasing molecular weight. It is also apparent that the activity is least for those fractions with the smallest number of naphthene rings but increases rapidly with increase in the average number of naphthene rings. There is a striking parallelism between specific rotation and specific refraction, the specific refraction passing through minima for those fractions where the rotations pass through maxima. Since there is no connection between specific refraction and specific rotation for substances in general, the parallelism pointed out here must have some significance peculiar to the composition of petroleum. As pointed out previously, the first fractions contain unsaturated hydrocarbons and probably aromatic hydrocarbons, and consequently it seems reasonable to suppose that the decrease in activity is due to the presence of unsaturated hydrocarbons or aromatics. If it is due to aromatic hydrocarbons it is interesting to speculate as to whether all aromatics in petroleum have low optical activities, or, as in the case of naphthenes, whether the activity depends on the number of rings in the molecule.

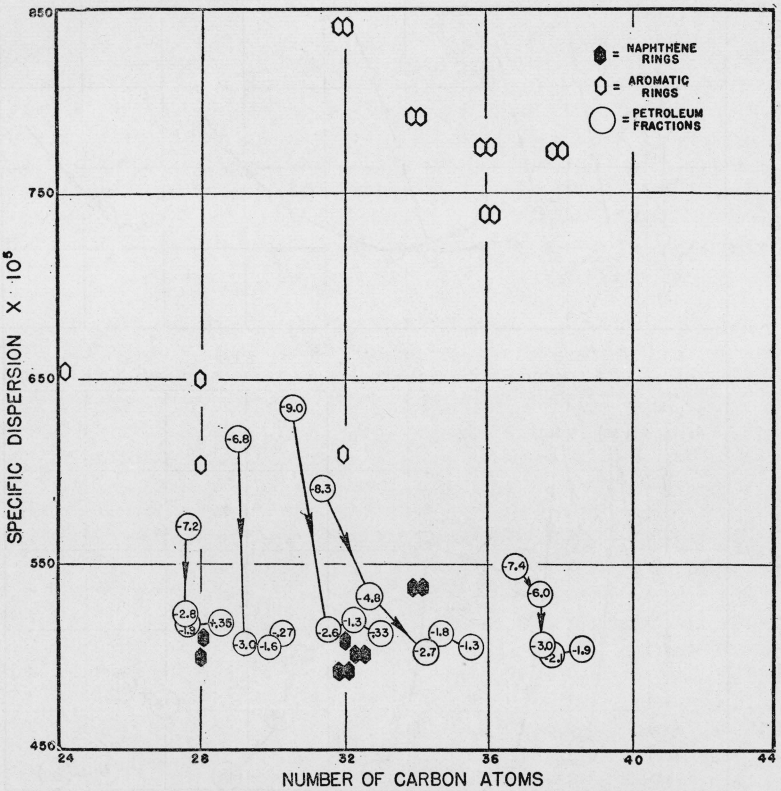

FIGURE 5.—*Specific dispersions of synthetic hydrocarbons and petroleum fractions.*

4. SPECIFIC DISPERSIONS

Another property used by Vlugter, Waterman, and Van Westen [12] for detecting the presence of aromatic hydrocarbons in petroleum oils is the specific dispersion. These authors point out that, as with specific refraction, the specific dispersion is highest for aromatics and lowest for naphthenes, decreasing with increase in the number of naphthene rings. In figure 5 are plotted values for the Lorentz-Lorenz specific dispersion

$$\frac{n^2_{F-1}}{n^2_{F+2}} - \frac{n^2_{c-1}}{n^2_{c+2}} \cdot \frac{1}{d}$$

for the key fractions from petroleum and for some of Mikeska's [1] synthetic hydrocarbons.[5] It is quite clear from a consideration of this property also that the first, and in a few instances the second, key fractions contain some aromatic or unsaturated hydrocarbons, but that in the remainder of the fractions the deviations of x in the formula C_nH_{2n+x} from the value +2 is due to the presence of naphthene rings.

5. ANILINE POINTS

In figure 6 is shown a plot of the aniline points[6] of the key fractions from petroleum with respect to the number of carbon atoms, fractions from each series being connected with arrows which denote the order of their extraction. There are also included values for a number of synthetic hydrocarbons. Lines drawn through each type of synthetic hydrocarbon indicate approximately the change in aniline point with molecular weight for that type. Unfortunately, aniline points for only three synthetic naphthenes are available. The aniline points for the two synthetic monocyclic naphthenes are somewhat lower (about 5° C) than the aniline points of the corresponding petroleum fractions, while the aniline point for the synthetic dicyclic is about 1° lower than that of the corresponding petroleum fractions. It is doubtful whether these differences are significant, as they may be due to differences in the technique employed in determining the aniline points—such as purity of aniline, etc. As with the other properties, the aniline points of the first key fractions are abnormal, being too low to be accounted for on the supposition that only naphthenes are present.

These data make evident the extreme importance of extracting fractions with a very narrow range of molecular weights if it is hoped to separate the various types of molecules. For example, judging from the aniline points of the key fractions, the aniline point of a dicyclic naphthene of 30 carbon atoms is about the same as that of a monocyclic with 28 carbon atoms. To effect a separation of monocyclic naphthenes from dicyclic naphthenes, by the use of solvents similar in behavior to aniline, it is almost necessary to use fractions composed entirely of hydrocarbons with the same number of carbon atoms. A monocyclic naphthene with 32 carbon atoms has about the same solubility as a monocyclic aromatic with 42 carbon atoms, so that even the separation of monocyclic aromatics from monocyclic naphthenes requires that the distillation range be not too wide. With

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[5] The dispersion values on the petroleum fractions, and those of Mikeska [1] on synthetic hydrocarbons, were obtained with an Abbe refractometer which gave values of $n_F - n_c$ instead of n_F and n_c, the properties required in this instance. To obtain the actual values of n_F and n_c use was made of Hartmann dispersion paper on which refractive indices for the different wave lengths are supposed to give a straight line. The validity of this procedure was checked by measuring the dispersion ($n_F - n_c$) for hexane, octane, and benzene, using the value for n_D given in International Critical Tables, and computing the values of n_F and n_c. The results agreed with the International Critical Tables values within 1 in the fourth decimal place for octane and benzene, and deviated by 2 in the fourth place for the F line of hexane. This method of calculation was suggested by C. P. Saylor of this Bureau.

[6] The aniline point is the temperature of complete miscibility of equal volumes of oil and aniline.

increase in the average number of naphthene rings in the key fractions the aniline point decreases and an extrapolation from the fractions composed of mono- and dicyclic naphthenes to the polycyclic naphthenes leads to the conclusion that the solubilities of six-ring naphthenes would not be far removed from the solubilities of monocyclic aromatics. So, to effect a separation of those classes by extraction

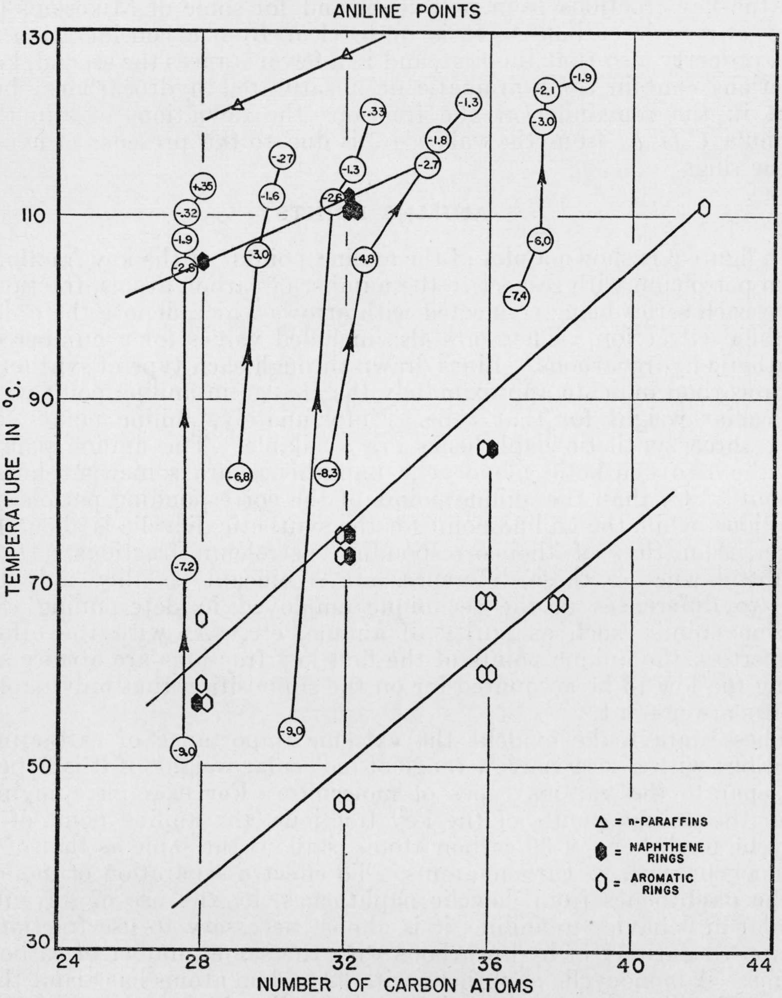

Figure 6.—*Aniline points of synthetic hydrocarbons and petroleum fractions.*

would require very narrow distillation fractions. This point will be referred to later.

6. VISCOSITY INDICES

The relationship between viscosity, the temperature coefficient of viscosity, and constitution have been investigated by many chemists, and is now much better understood than a few years ago. Hugel [14] and Mikeska [1], attacking the problem from the synthetic angle, have shown that increasing the degree of cyclization causes an increase in viscosity and a decrease in viscosity index. Davis and McAllister [11] found that a linear relationship exists between the viscosity index of an aromatic-free oil and the percentage of carbon atoms in naphthene rings, the viscosity index decreasing with increase in the percentage of carbon atoms in naphthene rings. They pointed out that the first extracts which they obtained from a Pennsylvania oil deviated from this linearity and explained this on the assumption that the first extracts contained aromatic or unsaturated hydrocarbons. It was of interest to test the relationship found by Davis and McAllister [11] with the key fractions obtained in this investigation. In the upper half of figure 7 is shown a plot of the percentage of carbon atoms

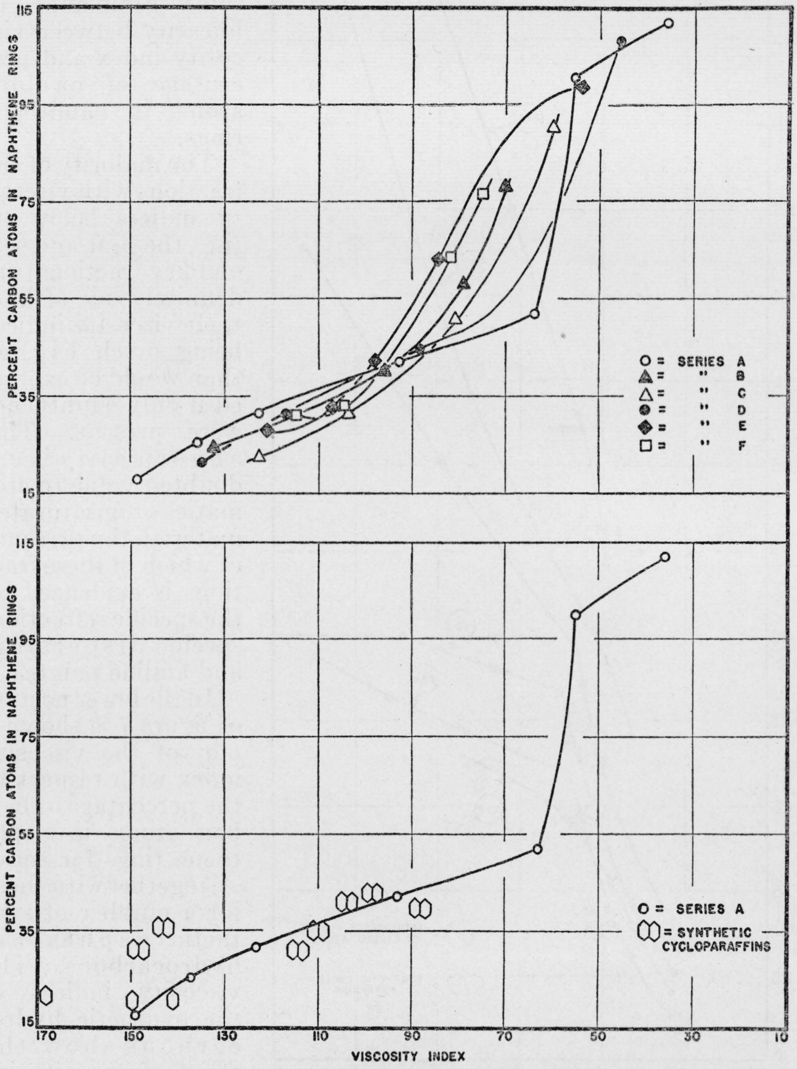

Figure 7.—*Viscosity indices of synthetic hydrocarbons and petroleum fractions.*

in naphthene rings (calculated from the empirical formulas on the assumption of six carbon atoms to the ring) with respect to the viscosity index. For oils with viscosity indices above 90 (although there is a marked scattering of points) there is some semblance of linearity between viscosity index and percentage of carbon atoms in naphthene rings.

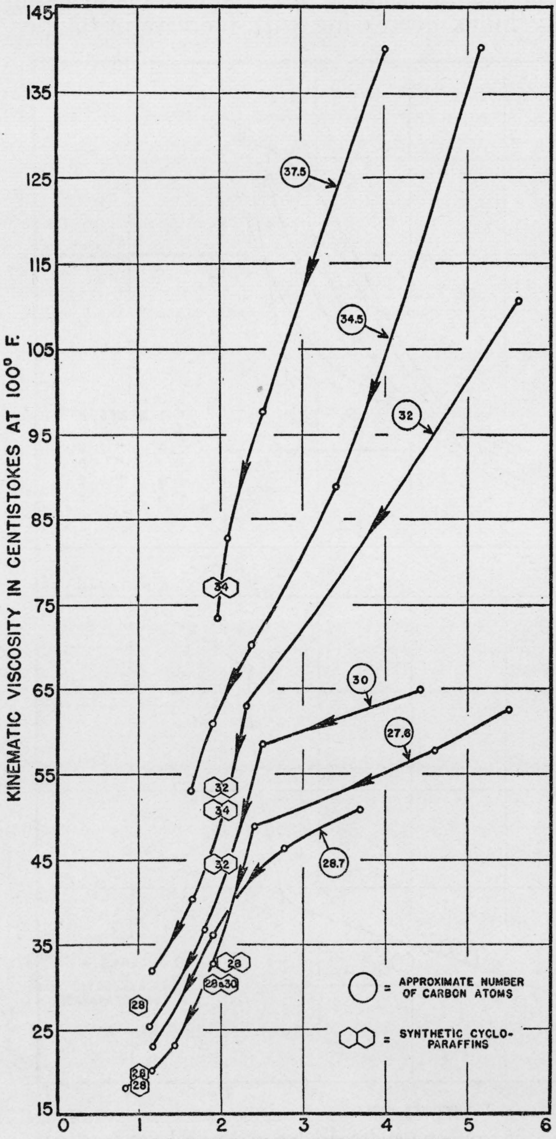

FIGURE 8.—*Viscosities of synthetic hydrocarbons and petroleum fractions.*

The majority of the fractions with viscosity indices below 90 (i.e., the first and second key fractions) are definitely out of line, their viscosity indices being much higher than would be expected if only naphthenes were present. This abnormality is undoubtedly due to aromatics or unsaturated material, the presence of which in these fractions is evidenced by the specific refraction, specific dispersion, and aniline points.

In the lower portion of figure 7 is shown a plot of the viscosity index with respect to the percentage of carbon atoms in naphthene rings for series *A*, together with those for a number of synthetic naphthenic hydrocarbons. The viscosity indices of the synthetic hydrocarbons show the effect of constitutive differences besides that of cyclization, but are in as good agreement with those of the fractions from petroleum as could be expected.

7. VISCOSITIES

In figure 8 are plotted the kinematic viscosities at 100° F of the key fractions from petroleum with respect to the number of rings they contain. The fractions from each extraction charge are connected with arrows which indicate the order of their extraction. The approximate number of carbon atoms in each series is indicated by the figures shown in the circles. Also represented in the figure by hexagons are a number of synthetic naphthenes, the figures within the hexagons indicating the number of carbon atoms contained in each naphthene. As has been observed by other investigators, both increase in molecular weight and increase in the degree of cyclization of the petroleum fractions cause an increase in the viscosity. As with the other properties, and presumably for the same reason (i. e., the presence of aromatic and unsaturated hydrocarbons), the first key fractions show abnormal viscosities, which were lower than expected. The synthetic naphthenes show the effect of constitutive differences other than cyclization, but are in as good agreement with the fractions from petroleum as could be expected.

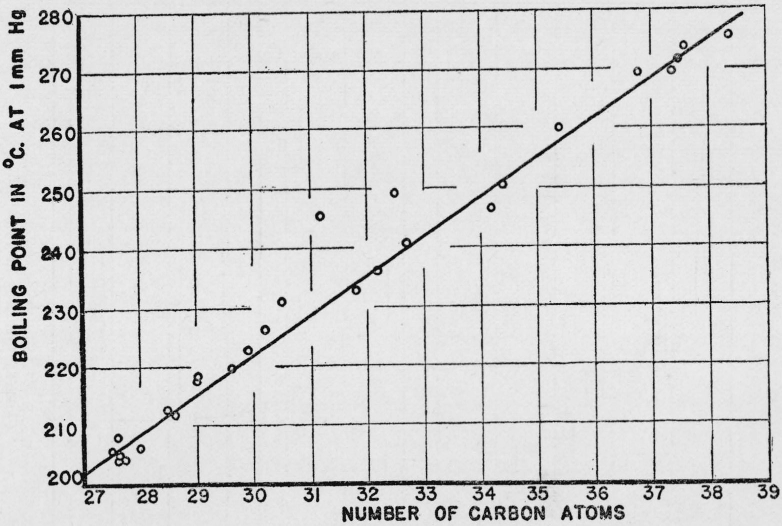

FIGURE 9.—*Relation between boiling point and number of carbon atoms of petroleum fractions.*

8. BOILING POINTS

In figure 9 are plotted the boiling points at 1 millimeter Hg pressure of the key fractions, with respect to the number of carbon atoms. A straight line represents the data fairly well, with the exception of two points.

As far as can be told from these data, the boiling point is a function of the number of carbon atoms and does not depend (at least to within about ±3° C) on the number of naphthene rings in the molecule.

V. EXAMINATION OF THE PROPERTIES OF THE FRACTIONS FROM SERIES *A*

In this discussion of physical properties and constitution, so far only the key fractions, on which a large number of physical properties were determined, have been considered. It is now in order to consider the properties of all the fractions from one charge. For this purpose the fractions from charge *A*, which was systematically extracted twice, will be considered. Charge *A* was divided into three equal parts (see fig. 1) and each part extracted separately. The resulting fractions were then blended according to their physical properties to make up three new charges, each of which was again extracted. In figures 10, 11, and 12 are plotted the refractive indices, viscosities, and viscosity indices of the fractions with respect to the percentage by weight of the charge for both the first and second extractions. The range in physical properties and total weight of the fractions which it was necessary to blend in preparation of the second set of charges are indicated at the right of the figures.

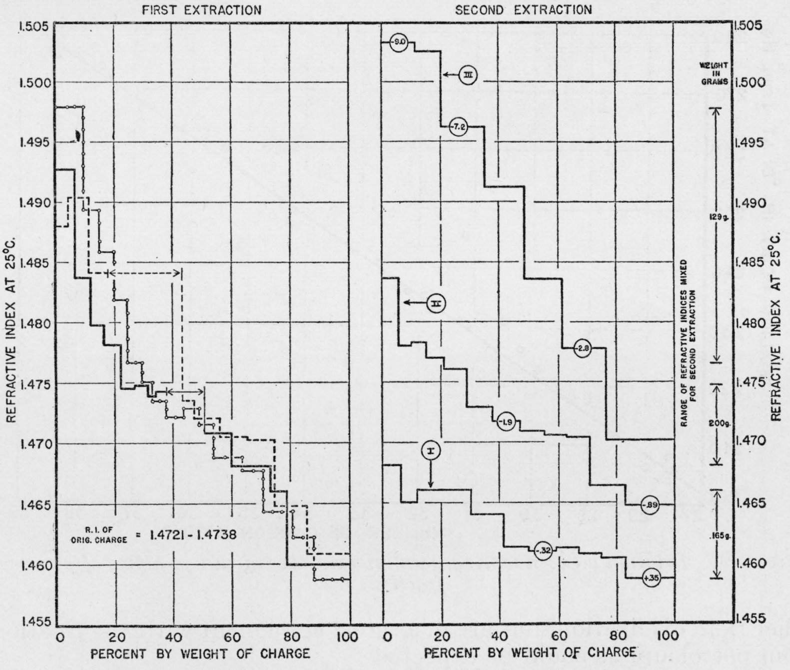

FIGURE 10.—*Refractive indices of fractions belonging to series A.*

The wide spread in the properties of the fractions from the first extraction is evident. The spread in properties of the fractions from each charge in the second extraction is less, and in the case of the less soluble fractions is scarcely more than the spread in properties of the fractions which were blended to make up the charge. This indicates that the limit of separation, with acetone as a solvent, and with the small charges available, has about been reached. There is a suggestion from the constancy of physical properties indicated by the flat portion of curves *I* and *II* that compounds of one type are concentrating in these regions, particularly since the empirical formulas in these regions correspond approximately to monocyclic and dicyclic naphthenes. One of the most interesting features of curve *III* is the fact that the viscosity decreases for the first few fractions, then rises markedly; the viscosity index also shows a similar peculiarity increas-

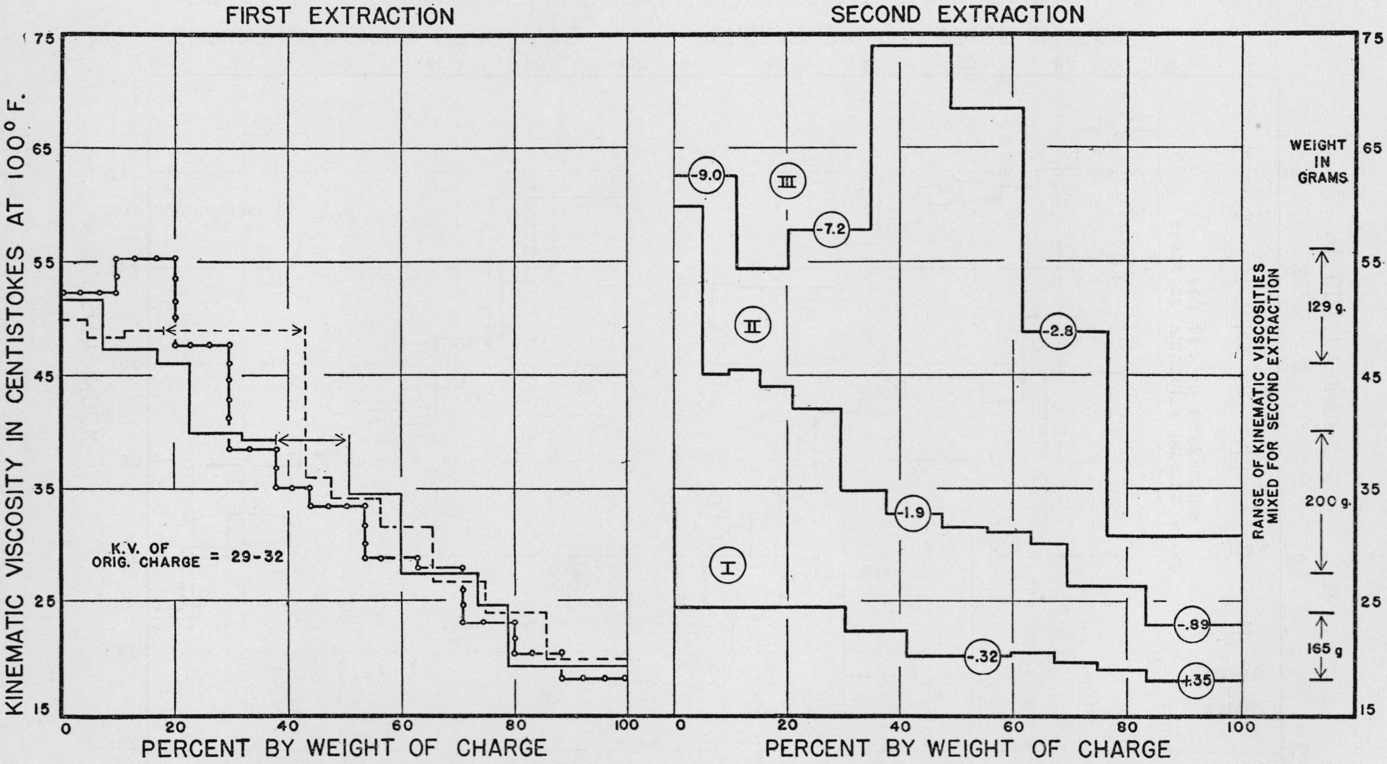

Figure 11.—*Viscosities of fractions belonging to series A.*

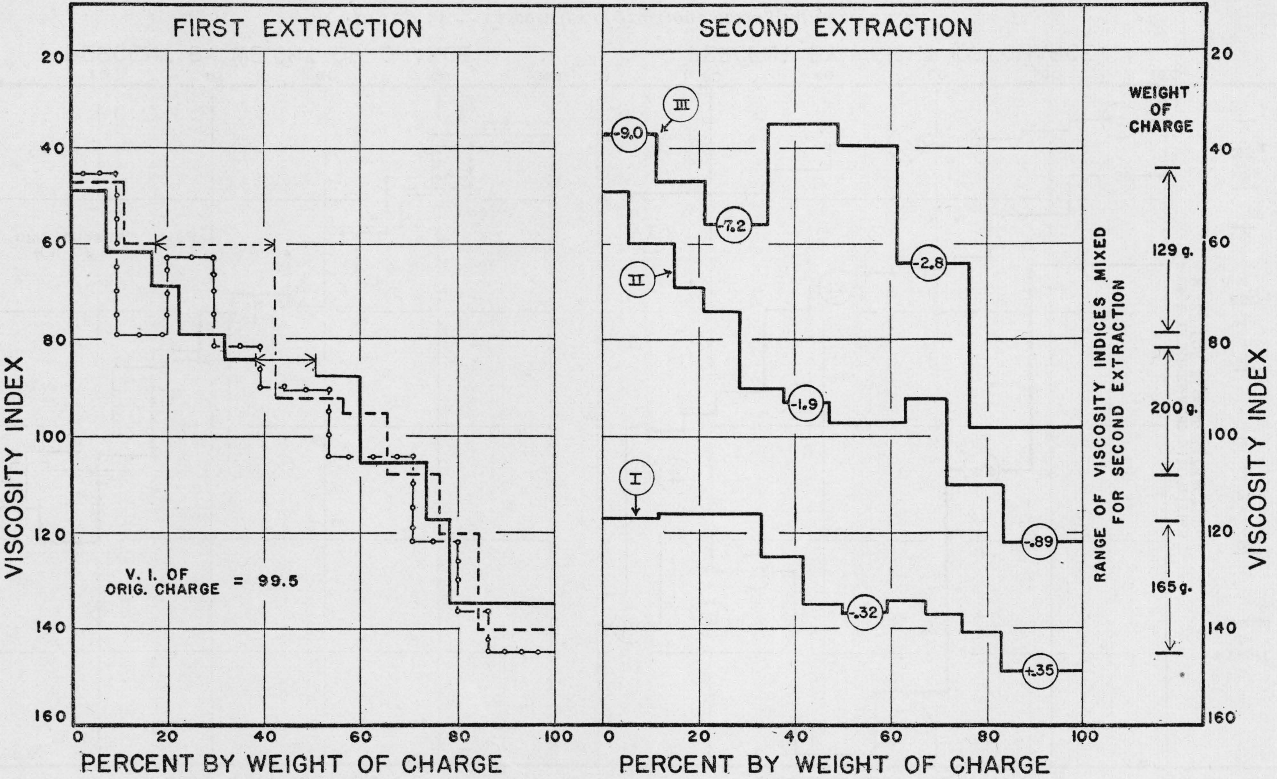

FIGURE 12.—*Viscosity indices of fractions belonging to series A.*

ing for the first few fractions, then decreasing markedly. These abnormal variations in viscosity and viscosity index are evidently not due to any change in the efficiency of the extracting column, since the refractive indices for these fractions decrease in a perfectly normal manner, but must instead be attributed to the fact that in this region we are dealing with a mixture of substances with markedly different viscosity characteristics. As has already been pointed out, the first fractions extracted contain small amounts of oxygen compounds, unsaturated material and probably aromatic hydrocarbons, and the abnormal viscosity characteristics are probably attributable to one or all of these substances.

Mikeska [1] has shown, from his study of the properties of synthetic compounds, that unsaturation does not appreciably change the viscosity characteristics. Therefore, if the unsaturated compounds in the first few fractions have the same composition (except for unsaturation) as the naphthenes contained in these fractions, then no abnormalities in viscosity would be expected. However, it is probable that the unsaturated material in these fractions is more nearly analogous in composition to the original charge, and consequently has a higher viscosity index and lower viscosity than the naphthenes in the fractions with which it occurs. This might account for the comparatively high viscosity indices and low viscosities of the first few fractions. The possibility that these anomalies are caused by aromatic hydrocarbons with high viscosity indices raises some interesting speculations which are considered in the succeeding paragraph.

VI. SPECULATION CONCERNING THE TEMPERATURE COEFFICIENT OF VISCOSITY OF THE AROMATIC EXTRACTS

Mikeska [1] has shown that in changing from a naphthene ring to an aromatic ring, without altering the rest of the molecule, there is some decrease in viscosity but no appreciable change in the viscosity index, and that aromatic hydrocarbons with one or two rings attached to long paraffin side-chains have, like the corresponding naphthenes, remarkably high viscosity indices. One might then naturally expect some material of high viscosity index in the supposedly aromatic extracts from petroleum. Yet to date no extract material of high viscosity index appears to have been found. Whether this material does not exist in petroleum, or whether its presence has been overlooked, is an interesting question. In figure 13 (curve *I*) are plotted the viscosity indices with respect to the number of rings in the molecule of the key fractions resulting from the double extraction to which reference has already been made. The 5 key fractions which contain no aromatics form a smooth curve which has been extrapolated to indicate (this requires experimental verification) what would be the viscosity index of a naphthene with 6 rings and 28 carbon atoms. On the basis of Mikeska's conclusions just referred to, curve *II* has been constructed identical in shape with curve *I* and indicates what would be the viscosity indices of aromatics analogous in constitution to the naphthenes of curve *I*. Curve *II* is displaced from curve *I* in such a manner that monocyclic aromatics fall above hexacyclic naphthenes. If aromatics with one ring have solubilities not far removed from those naphthenes with six rings (as was indicated to be probable in the discussion of aniline points on p. 932), it is easy to see why aromatic extracts of high viscosity index have not been obtained. In the modern methods fractions with wide boiling ranges are extracted, and the mononuclear aromatics of high viscosity index would always be mixed with polynuclear naphthenes of low viscosity index. This question, in addition to its theoretical interest, is of considerable practical importance, since the petroleum industry today may be discarding, in the solvent extraction processes, aromatic material with viscosity characteristics as good as the best naphthenic material and with oxidation characteristics which may be as desirable.

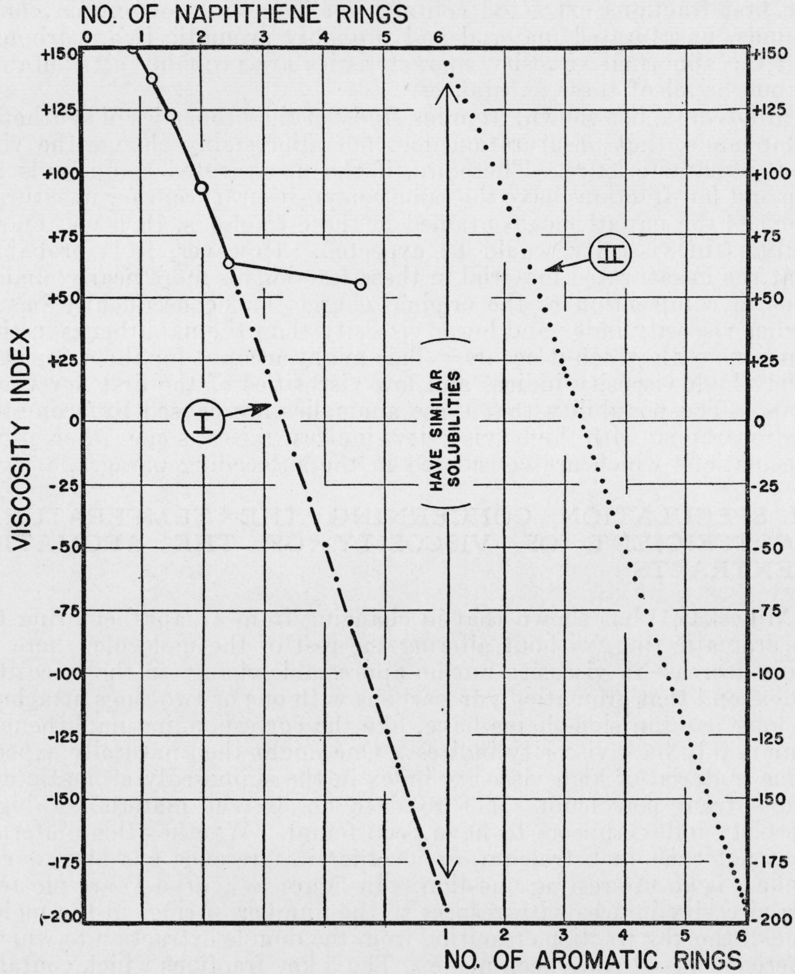

FIGURE 13.—*Relation between viscosity index and number of rings for cycloparaffins and for aromatic hydrocarbons.*

VII. THE QUESTION OF THE PRESENCE OF ISO- OR BRANCHED-CHAIN PARAFFINS IN LUBRICATING OIL

Whether iso- or branched-chain paraffins are an important constituent of mineral oils is a question concerning which there have been differences of opinion. Kyropoulos [15] came to the conclusion, as a result of comparing the refractive indices and densities of fractions of a Pennsylvania oil with those of synthetic hydrocarbons, that it was composed largely of isoparaffins. Vlugter, Waterman, and Van Westen, considering the same data on the same oils, show that the specific refractions are too low to be accounted for on the assumption of the presence of isoparaffins, and concluded that these oils are composed of naphthenes. An examination of the literature shows that of the many fractions of wax-free lubricating oils from a wide variety of sources, and prepared by widely different methods, none have been found with a positive value of x in the formula C_nH_{2n+x}. An examination of the key fractions used in this investigation shows only one fraction with a positive value for x ($x=+0.35$) in the formula C_nH_{2n+x}. This fraction contained a small amount of wax, which was removed and identified from its melting point and refractive index as being composed of normal paraffin hydrocarbons. Negative values for x do not, however, prove the absence of isoparaffins, since mixtures of a dicyclic naphthene with an isoparaffin may give negative values for x. Nevertheless, the fact that there were observed no fractions richer in hydrogen than C_nH_{2n}, (except for that one known to contain normal paraffins) obtained from an extraction process which was definitely separating the oil into fractions containing respectively more or fewer naphthene rings, and which should consequently have separated isoparaffins, is considered strong evidence that no appreciable percentage of isoparaffins exists in these fractions.

Indeed, even the supposed existence of isoparaffins in wax from petroleum needs reexamination, since the determination of the empirical formulas of some waxes in this laboratory [16] has shown that certain waxes melting some 35° C below the corresponding normal paraffins, and which formerly were supposed to consist of isoparaffins, show considerable deficiencies in hydrogen from the formula C_nH_{2n+2}.

VIII. CONCLUSION

From the comparisons and analyses which have been made in the preceding pages, the following conclusions may be drawn.

1. The least soluble portion of the oil—that is, the material corresponding to the most highly refined product obtained by any good solvent-extraction process, consists substantially of naphthenes (cycloparaffins) containing from one to about three rings to the molecule together with the necessary alkyl radicals. The somewhat more soluble portion consists of naphthenes with more rings, together with some unsaturated hydrocarbons and possibly some aromatic hydrocarbons.
2. There is no evidence whatever for the existence of iso- or branched-chain paraffins in the lubricating oil from midcontinent crude.
3. Because of the similar solubility relations, it is possible that, in the extraction processes as used at the present time one-ring aromatic hydrocarbons are being discarded to waste along with the undesirable naphthenes containing about six rings to the molecule. This is a point well worth investigating, since these one-ring aromatic hydrocarbons may be a valuable constituent for good lubricating oil.

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