Studies on the Micro-paraffins. V. X-Ray Investigation of Various Paraffin Waxes

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Fundamental studies of micro-paraffins performed previously by the present author have revealed that the formation of fine crystal grains of micro-paraffin is not an essential character of micro-paraffin itself[1-3]. It has been found that the existence of a small amount of a certain compound seems to be the cause of the formation of fine crystal grains. In order to verify this point, an X-ray investigation of various paraffins seems to be necessary.

There have been many reports on X-ray diffraction of *n*-paraffin. Müller reported[4] that the cell dimensions of *n*-paraffin (carbon number 29) are $a=7.45$ Å, $b=4.97$ Å, and $c=79.2$ Å. Bunn[5] studied the crystal structure of long-chain normal paraffin hydrocarbons and, in particular, examined the "shape" of $>CH_2$ groups. Furthermore, many data on the X-ray diffraction of *n*-paraffin were introduced by Francis and Piper[6].

The present paper deals with the X-ray diffraction of *n*-dotriacontane (carbon number 32), various paraffin waxes (commercial products), micro-paraffins (commercial products), the micro-paraffin obtained from the tank residue of Aramco crude oil in Saudi-Arabia, and each fraction of micro-paraffin separated by the urea method and chromatography. The chain length, the lengths of a- and b-axes, the cross-sectional area occupied by one paraffin molecule, molecular volume, etc. were determined from the peak in the X-ray diffraction curve. There were a few interesting phenomena and observations on X-ray diffraction when some agents with a O-H group and a benzene ring were added to *n*-dotriacontane.

Experimental

Sample of Paraffin.—The following samples were used as described in the former reports: various paraffin waxes (commercial products), micro-paraffins (commercial products), refined *n*-dotriacontane, the micro-paraffin obtained from the tank residue of Arabian crude oil, and each fraction of micro-paraffin separated by the urea method and chromatography.

Measurement of X-Ray Diffraction.—An X-ray diffractometer (Geiger Flex, manufactured by Rigaku Denki Co.) was used for the measurement of the X-ray diffraction. The sample was placed on a glass plate, melted by heating to 70~75°C (a little higher than its melting point), and kept standing at room temperature (15~20°C), then the solidified sample was placed in the apparatus for the measuremen of the X-ray diffraction. When *n*-dotriacontane, to which substances such as "Santopour", picric acid, *p*-hydroxydiphenyl, asphalt components, etc. had been added, was taken as a sample, it was dissolved in ethyl alcohol and the crystals, formed by cooling gradually to room temperature, were filtered and measured after drying, as in the above operation.

At first, preliminary measurements were made in the range of 0~90° (2θ), in order to fix the range of the diffraction angle where (100) and (200) peaks appeared. Then the diffraction curves were carefully recorded for the range where the main peaks appeared.

The scale of the diffraction angle (2θ) was calibrated by using a standard sample (quartz)[7] and was measured under the conditions shown in Table I.

It was found by preliminary measurement that the peak due to (001) appeared at an angle less than

Table I. Conditions for the measurement on the (110) and (200) peaks

	a_1	b_1
Target	Fe	Cu
Filter	Mn	Ni
Scanning speed (deg./min.)	1/4	1/4
Chart speed (cm./min.)	1	1

Table II. Conditions for the measurement on the (100) peak

	a_2	b_2
Target	Fe	Cu
Filter	Mn	Ni
Scanning speed (deg./min.)	1(1/4)	1
Chart speed (cm./min.)	1	1

1) K. Negoro, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 295 (1961).
2) K. Negoro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 230 (1961).
3) K. Negoro, This Bulletin, **34**, 1366 (1961).
4) A. Müller, *Proc. Roy. Soc.*, **A120**, 455 (1928).
5) C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).
6) F. Francis and S. H. Piper, "Science of Petroleum", Vol. II, Ed. by A. E. Dunstan et al., Oxford University Press, London (1938), p. 1203.
7) K. Kubo and S. Kato, "Chemical Analysis by X-Ray Diffraction", Nikkan Kogyo, Tokyo (1955), p. 302.

5°; the measurement of this peak was made under the conditions shown in Table II (Almost all of these experiments were made by using CuK_α radiation). In this case, various paraffin samples, the surfaces of which were cut smooth with a microtome and cut to suitable thickness with a knife, were placed on the glass by means of Scotch tape.

Results and Discussion

The Spacings d_{110} and d_{200}.—From the peak of each X-ray diffraction curve of the various paraffins obtained by FeK_α or CuK_α radiation, the spacings d_{110} and d_{200} were computed by Bragg's equation. The results are shown in Table III.

The results obtained by FeK_α and CuK_α radiation were markedly similar, as is shown in Table III repeatability.

n-Dotriacontane or pure *n*-hydrocarbon (carbon number 32) has the value of 4.15 Å for d_{110} and of 3.77 Å for d_{200}. The crystalline paraffin (m. p. 53.5°C), a mixture of various hydrocarbons, has the value of 4.19 Å for d_{110}; in other words the spacing is increased. Moreover, in the case of micro-paraffin, the product obtained from the tank residue of Aramco crude oil and the commercial one both have the value of 4.16 Å for d_{110}, which is slightly larger than that of *n*-dotriacontane.

Table III. The spacings d_{110} and d_{200} of various paraffins

Name	Radiation	2θ	d_{110}, Å	2θ	d_{200}, Å
n-Dotriacontane	FeK_α	26°58′	4.15	29°48′	3.77
n-Dotriacontane	CuK_α	21°24′	4.15	23°39′	3.76
Crystalline paraffin (m. p. 53.5°C)	FeK_α	26°44′	4.19	29°42′	3.78
Crystalline paraffin (m. p. 53.5°C)	FeK_α	26°42′	4.19	29°41′	3.78
Micro-paraffin	FeK_α	26°56′	4.16	29°59′	3.75
Micro-paraffin (de-asphalted)	FeK_α	26°53′	4.16	29°51′	3.76
Micro-paraffin (de-asphalted)	FeK_α	26°53′	4.16	29°51′	3.76
Micro-paraffin (de-asphalted)	CuK_α	21°18′	4.17	23°39′	3.76
Micro-paraffin (Shell)	FeK_α	26°54′	4.16	29°56′	3.75
Micro-paraffin (Shell)	FeK_α	26°54′	4.16	29°57′	3.75
Micro-paraffin (commercial)	FeK_α	26°56′	4.16	29°59′	3.75
Micro-paraffin urea adducts	FeK_α	26°54′	4.16	29°50′	3.76
Micro-paraffin urea adducts	CuK_α	21°18′	4.17	23°42′	3.75
Micro-paraffin urea rejects	FeK_α	26°39′	4.20	29°35′	3.80
Micro-paraffin urea rejects	CuK_α	21°05′	4.21	23°25′	3.80
Micro-paraffin pentane fraction	FeK_α	26°45′	4.19	29°42′	3.78
Micro-paraffin pentane fraction	CuK_α	21°09′	4.20	23°30′	3.79
Micro-paraffin benzene fraction	FeK_α	26°44′	4.19	29°42′	3.78
Micro-paraffin benzene fraction	CuK_α	21°09′	4.20	23°33′	3.78
Micro-paraffin alcohol fraction	FeK_α	—***	—	—	—
Micro-paraffin alcohol fraction	CuK_α	—	—	—	—
Micro-paraffin (commercial) pentane fraction	FeK_α	26°55′	4.16	29°58′	3.75
Micro-paraffin (commercial) benzene fraction	FeK_α	26°48′	4.18	29°49′	3.77
Micro-paraffin (commercial) alcohol fraction	FeK_α	—	—	—	—
Micro-paraffin adducts pentane fraction	FeK_α	26°57′	4.16	29°56′	3.75
Micro-paraffin adducts pentane fraction	CuK_α	21°23′	4.15	23°37′	3.76
Micro-paraffin adducts benzene fraction	FeK_α	26°48′	4.18	29°49′	3.77
Micro-paraffin adducts benzene fraction	CuK_α	21°16′	4.17	23°34′	3.78
Micro-paraffin adducts alcohol fraction	FeK_α	26°52′	4.17	—	—
Micro-paraffin adducts alcohol fraction	CuK_α	21°17′	4.17	23°39′	3.76
Micro-paraffin rejects pentane fraction	FeK_α	26°43′	4.19	29°42′	3.78
Micro-paraffin rejects pentane fraction	CuK_α	21°08′	4.20	23°27′	3.80
Ar wax*	FeK_α	26°52′	4.17	29°50′	3.76
Amber wax**	FeK_α	26°53′	4·16	29°54′	3.75
Paraffin (PE added) (base crystalline paraffin)	FeK_α	26°45′	4.19	29°44′	3.78
"Santopour" added *n*-dotriacontane	FeK_α	—	—	—	—
Picric acid added *n*-dotriacontane	FeK_α	—	—	—	—
p-Hydroxydiphenyl added *n*-dotriacontane	FeK_α	—	—	—	—
Asphalt added *n*-dotriacontane	FeK_α	—	—	—	—

* Paraffin product to which polyethylene was added.
** Micro-paraffin product to which polybutene was added.
*** — does not show any peak in the X-ray diffraction curve.

It was noticed that the values for d_{110} and d_{200} of the paraffin, about 62% of which formed urea adducts, were vary similar to those of *n*-paraffin when obtained from micro-paraffin by the urea method.

Consequently, though it has been stated that micro-paraffin consists of side-chain paraffins[8] it may be certain from the above results that some straight-chain hydrocarbons are possibly also contained in it.

The value for d_{110} of the remainder of the paraffin forming usea rejects in micro-paraffin was as large as 4.21 Å, and the value for d_{200} increased to 3.80 Å. It seems likely that these parts of micro-paraffin were rich in side-chain hydrocarbons.

When micro-paraffin was directly separated by chromatography, no great difference was observed between the pentane and benzene fractions, and its alcohol fraction was amorphous, for the peak on the X-ray diffraction curve was not observed. However, when micro-paraffin was separated into urea adducts and rejects by the urea method, the fractions of pentane, benzene and alcohol, separated by chromatography, showed remarkable differences.

When substances such as "Santopour", picric acid, *p*-hydroxydiphenyl, asphalt components, etc., were added to *n*-dotriacontane, the peaks (110) and (200) were not clearly observed. Therefore, it appeared that the product became amorphous.

Chain Lengths of Various Paraffins.—From the peak of (001), the chain lengths of carbon of various paraffin samples were computed by Bragg's equation. The results are listed in Table IV. The relation between the chain length and the carbon number of *n*-paraffin is given by the following Eq. 1 obtained by Kurtz and Lipkin[9].

$$\text{Å} = 1.27\, N_1 + 2.0 \qquad (1)$$

where Å is chain lengh in Å and N_1 is carbon number.

Column "a" in Table IV shows the values of N_1 computed by the values of chain length in Eq. 1. If N_1 were calculated by Eq. 1 from the results of the X-ray diffraction of refined *n*-dotriacontane (carbon number 32), its value would be

$$31.7 \fallingdotseq 32$$

Accordingly, it was recognized that the above value nearly agreed with the theoretical one.

In fact, the constant (2.0) in the above equation was in the range of 2.0~3.5 according to the preparation methods of samples as reported by Piper et al.[10] and Müller[11].

It was reported[12] that the lowest value (approximately 2) was obtained when *n*-paraffin, crystallized on a glass plate, was measured by X-ray diffraction. The constant was computed by Eq. 1 at 1.7 from the chain length of *n*-dotriacontane (42.3 Å) and the theoretical value of carbon number (32). Thus, Eq. 1 can be written as follows:

$$\text{Å} = 1.27\, N_1 + 1.7 \qquad (2)$$

TABLE IV. CHAIN LENGTHS OF VARIOUS PARAFFINS

Name	2θ(°)	Chain length Å	Carbon number of chain a	Carbon number of chain b
n-Dotriacontane	2.09	42.3	31.7	32.0
Crystalline paraffin (m. p. 53.5°C)	2.38	37.1	27.7	27.9
Crystalline paraffin (m. p. 60.0°C)	2.08	42.0	31.4	31.7
Crystalline paraffin urea adducts (m. p. 53.5°C)	2.42	36.8	27.4	27.6
Crystalline paraffin urea rejects (m. p. 53.5°C)	2.36	37.8	28.2	28.5
Micro-paraffin	1.20	50.8	38.4	38.6
Micro-paraffin (de-asphalted)	1.48	48.5	36.6	36.8
Micro-paraffin urea adducts	1.70	46.4	34.9	35.2
Micro-paraffin urea rejects	1.21	50.7	38.3	38.5
Micro-paraffin pentane fraction	1.61	47.3	35.6	35.9
Micro-paraffin urea adducts pentane fraction	1.75	45.9	34.5	34.8
Micro-paraffin urea rejects pentane fraction	1.56	47.8	36.1	36.3
Micro-paraffin (commercial)	1.00	53.2	40.3	40.5
Micro-paraffin (Shell)	1.38	49.4	37.3	37.5
Ar wax	2.39	37.0	27.5	27.8
Amber wax	1.18	49.1	37.0	37.3

8) B. T. Brooks, C. E. Board, S. S. Kurtz and L. Schmerling, "The Chemistry of Petroleum Hydrocarbon", Reinhold Publ. Corp., New York (1954).
9) S. S. Kurtz, Jr. and M. R. Lipkin, *Ind. Eng. Chem.*, **33**, 779 (1941).
10) S. H. Piper, D. Brown and S. Dwyment, *J. Chem. Soc.*, **127**, 2194 (1925).
11) A. Müller and W. B. Saville, ibid., **127**, 599 (1925).
12) "Chemistry of Petroleum Hydrocarbons", Vol. II, Kyoritsu Shuppan, Tokyo (1956), p. 2

Table V. Values of constant (k), when those substances which were considered to have micro-crystallization effects were added to n-dotriacontane

Name	2θ(°)	Chain length Å	Constant number k
Base (n-dotriacontane)	2.09	42.3	1.7
n-Dotriacontane (picric acid added)	2.05	43.1	2.5
n-Dotriacontane (" Santopour " added)	2.01	44.0	3.4
n-Dotriacontane (p-hydroxydiphenyl added)	2.05	43.1	2.5
n-Dotriacontane (asphalts added)	2.06	42.9	2.3

Column " b " in Table IV shows the values of the carbon numbers of various paraffins computed by Eq. 2.

As shown in Table IV, it was recognized that the micro-paraffin consisted of long carbon chain hydrocarbons and that the chain length was in the range 47~53 Å, while the value for crystalline paraffin was 36~42 Å.

As for the carbon number of the chain, it was found that the value for micro-paraffin was considerably larger, 37~40, assuming that it was in the fully extended chain state, while the value for crystalline paraffin was 27~32. The straight paraffin obtained from the micro-paraffin by the urea method was C_{35}; therefore, its carbon chain was shorter than that of the base paraffin.

On the contrary, it was recognized that the carbon number of the urea non-adducts was slightly larger than that of the base paraffin, when the value was computed assuming that the paraffin was in the fully extended chain state even though it was actually rich in side chain hydrocarbons.

As reported in the previous paper,[3] when " Santopour ", picric acid, p-hydroxydiphenyl and asphalt components, nemely those compounds which were considered to have micro-crystallization effects, were added to n-dotriacontane, (110) the peak shifted to the smaller angle of 2θ, indicating that the chain length increased compared only with the case of n-dotriacontane of the base paraffin. In this case, the constant (2.0) of Eq. 1 was replaced by k:

$$\text{Å} = 1.27\, N_1 + k \qquad (3)$$

The value of k was computed by replacing $N_1 = 32$ and the observed value of the chain length (Å), the results being shown in Table V.

The larger values of k in Table V suggest that the crystal lattice has a certain disorder, and it was noticed that " Santopour " had the largest effect on the crystal of n-dotriacontane with the largest value of k.

X-Ray Diffraction Pattern of d_{001} and Crystallinity.—The X-ray diffraction curves of typical paraffins are shown in Fig. 1, in which intensity is in ordinate and the diffraction angle (2θ) is in abscissa. As for the crystalline paraffin or n-dotriacontane, various orders of reflections of (001) were observed, but for the micro-paraffin, it was noticed that only the first order appeared. If " Santopour ", picric acid, p-hydroxydiphenyl, etc., or those substances having micro-crystallization effects, were added to n-dotriacontane, it was found that all the higher order reflections disappeared.

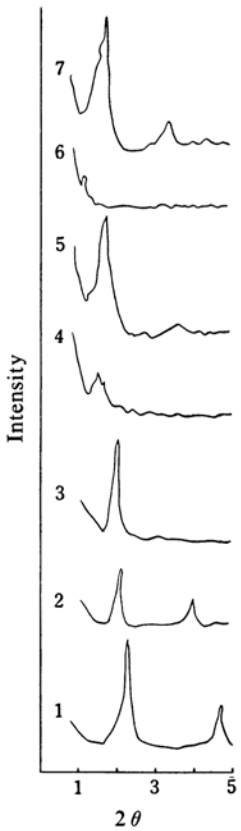

Fig. 1. X-Ray diffraction curve of typical paraffins.
1. Crystalline wax (m. p. 53.5°C)
2. n-Dotriacontane
3. n-Dotriacontane (" Santopour " added)
4. Micro-paraffin
5. Micro-paraffin urea adducts
6. Micro-paraffin urea rejects
7. Micro-paraffin urea adducts pentane fraction

Table VI. Length of a and b axes, cross-sectional area of one molecule (S), and ϕ of various paraffins

Name	a, Å	b, Å	S, cm²	ϕ
n-Dotriacontane	7.54	5.03	19.0×10^{-16}	67°24′
Crystalline wax (m. p. 53.5°C)	7.56	5.04	19.1×10^{-16}	67°22′
Micro-paraffin	7.50	5.00	18.8×10^{-16}	67°30′
Micro-paraffin (de-asphalted)	7.52	5.00	18.8×10^{-16}	67°14′
Micro-paraffin (Shell)	7.50	5.01	18.8×10^{-16}	67°30′
Micro-paraffin (commercial)	7.50	5.01	18.8×10^{-16}	67°30′
Micro-paraffin urea adducts	7.52	5.00	18.8×10^{-16}	67°14′
Micro-paraffin urea rejects	7.60	5.05	19.2×10^{-16}	67°12′
Micro-paraffin pentane fraction	7.56	5.04	19.0×10^{-16}	67°22′
Micro-paraffin adducts pentane fraction	7.50	5.01	18.8×10^{-16}	67°30′
Micro-paraffin rejects pentane fraction	7.56	5.04	19.0×10^{-16}	67°22′
Ar wax	7.52	5.01	18.8×10^{-16}	67°20′
Amber wax	7.50	5.01	18.8×10^{-16}	67°30′

When micro-paraffin was reacted with urea, the straight paraffin (urea adducts paraffin) thus obtained showed (001) and a very weak (002). However, the pentane fraction, obtained from the urea adducts by chromatography, showed higher order reflections clearly, and it was found that the crystalline state gradually had a resemblance to that of *n*-paraffin. On the contrary, in the case of urea rejects of paraffin, such peaks did not appear at all. As mentioned above, the appearance of the peaks on X-ray diffraction curves has some relation with the crystallinity of paraffins in actuality, and it is interesting that the details of the X-ray dffraction pattern of micro-paraffin have been made clear, and that the effects of "Santopour" etc., or those compounds with an O–H group and benzene ring, have been observed on the change which occurred in the peaks on the X-ray diffraction curve.

Length of a- and b-Axes and Cross-sectional Area of Various Paraffin Crystals.—Müller[13] studied the X-ray diffraction of *n*-paraffin, and the cross-section of the unit cell is shown in Fig. 2. It was confirmed that one paraffin chain was in the center of unit cell and that a paraffin chain with a different azimuthal orientation was at each of the four corners of the unit cell.

For the packing of paraffin molecules, no experimental evidence was obtained for any kind of paraffins; however, according to Müller, it would be proper to consider that each crystal had a cross-section as shown in Fig. 2 and a c-axis perpendicular to it. The length of the a- and b-axes, the cross-sectional area occupied by one molecule (S), and ϕ were computed from the values for d_{110} and d_{200} by the following Eqs. 4—7. The calculated values are shown in Table VI, and part of the values which Müller reported on *n*-paraffins of various carbon numbers are reproduced in Table VII.

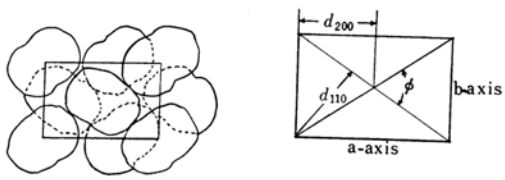

Fig. 2. Cross-section of unit cell.

$$a=2\cdot d_{200} \tag{4}$$

$$b=a\cdot d_{110}/\sqrt{a^2-(d_{110})^2} \tag{5}$$

$$c=a\cdot b/2 \tag{6}$$

$$\tan\phi/2=b/a \tag{7}$$

Table VII. Length of a and b axes, cross-sectional area of one molecule (S), and ϕ of various *n*-paraffins (Müller)

Number of carbon atoms	a, Å	b, Å	S, cm²	ϕ
19	7.55	5.01	18.9×10^{-16}	67°10′
24	7.41	4.94	18.3×10^{-16}	67°20′
29	7.42	4.94	18.3×10^{-16}	67°16′
30	7.33	4.92	18.2×10^{-16}	67°44′
31	7.40	4.93	18.2×10^{-16}	67°15′
34	7.40	4.95	18.3×10^{-16}	67°30′
44	7.33	4.93	18.1×10^{-16}	67°52′

The length of the a- and b-axes of *n*-dotriacontane (*n*-paraffin of carbon number 32) had slight differences of 0.14 Å and 0.10 Å compared with the values for *n*-paraffin (carbon number 31) of Müller; it was also recognized that the values for various paraffins were almost similar. As for the cross-sectional area occupied by one molecule, the values for various paraffins were in the range of $(18.8\sim19.2)\times10^{-16}$ cm², and it was recognized that no great differences were to be seen among various paraffins, assuming that they were in normal crystal form, though

13) A. Müller, *Proc. Roy. Soc.*, **A128**, 514 (1932).

the urea adducts of paraffins showed somewhat larger values than those of the other paraffins.

Molecular Volume of Various Paraffins. — When the chain length and the cross-sectional area occupied by one molecule have been computed, the molecular volume of various paraffins may be calculated by the following equation, assuming that they are *n*-paraffins:

$$V = d_{001} \cdot ab/2 \qquad (8)$$

Table VIII shows the molecular volume (Å^3/mol.) of various paraffins calculated from Eq. 8.

TABLD VIII. MOLECULAR VOLUME OF VARIOUS PARAFFINS

Name	Molecular volume, Å^3
n-Dotriacontane	804
Crystalline wax (m. p. 53.5°C)	708
Micro-paraffin	955
Micro-paraffin (de-asphalted)	911
Micro-paraffin (Shell)	928
Micro-paraffin (commercial)	998
Micro-paraffin urea adducts	872
Micro-paraffin urea rejects	974
Micro-paraffin pentane fraction	900
Micro-paraffin adducts pentane fraction	867
Micro-paraffin rejects pentane fraction	909
Ar wax	695
Amber wax	923

The molecular volume of *n*-paraffin was computed from carbon number (N_1) by the following equation:

$$V = 23.50\, N_1 + 37.0 \qquad (9)$$

For *n*-dotriacontane the molecular volume, calculated by putting $N_1 = 32$ in Eq. 9, was 789, while that computed from X-ray diffraction data by Eq. 8, was 804. The difference between these two is 15, that is, approximately 2%. As for the micro-paraffin, a mixture of various hydrocarbons, the value of the molecular volume is not accurate, but this might give some clue as to the molecular volume.

Summary

From the X-ray diffraction of *n*-dotriacontane, various paraffin waxes, micro-paraffin, and each fraction of micro-paraffin separated by the urea method and chromatography, the chain length and the spacings (110) and (200) of each crystal have been computed. Furthermore, the carbon number of the chain, the lengths of the a- and b-axes, the cross-sectional area occupied by one molecule, and the molecular volume have been calculated. They have been calculated on the assumption that thay were in normal crystal form, but in order to make it exact, it is necessary to work with a single crystal. The author would like to try further experiments.

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