Studies on Micro-paraffin. III. Properties and Spectra of Each Fraction of Micro-paraffin Separated by Urea Method and Chromatography

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Since Bengen's discovery in 1940[1,2], it has been observed with interest that crystalline molecular compounds, that is to say, urea adductible components, were formed by urea and organic compounds of straight-chain structure and numerous studies on this reaction have been reported. The application of this reaction has been remarkably developed as one of the excellent separation methods of organic compounds[3]. Phillips[4] explained that 20~90% of urea adductible compenents were contained in microcrystalline waxes.

Molecular compounds, formed by urea and ordinary paraffin waxes, were previously reported[5,6], and the studies on micro-paraffins will be explained in this report. The micro-paraffin was separated into two groups of compounds; one was of the straight-chain structure forming adducts with urea and the other was of the non-straight-chain structure forming no adducts. Then, each group was separated into three fractions soluble in pentane, benzene, and alcohol, successively, by chromatography with silica gel. The crystal properties of each soluble fraction were studied and its ultraviolet and infrared absorption spectra were measured.

As a result of these experiments, it was confirmed that it was reasonable to consider that the cause of the micro-crystallization of the so-called micro-paraffin should be not essential, but derived by secondary factor. It was also confirmed that about 60% of the micro-paraffins obtained from the tank residue of Arabian crude oil (Aramo oil in Saudi-Arabia)[7] consisted of urea adductible paraffins which had higher melting points and lower refractive indices than those of non-adductible ones. However, it was found when the ultraviolet spectra of each soluble fraction was separated by chromatography that small quantities of various aromatics were mixed with the fractions and an absorption band due to the double band was observed on the infrared

1) F. Bengen, German Pat. O. Z 12438 (1940).
2) F. Bengen, *Angew. Chem.*, **63**, 207 (1951).
3) "The Chemistry of Petroleum Hydrocarbons" (Sekiyu Tankasuiso Kagaku) I, Kyoritsu Shuppan Co., Tokyo (1956), p. 26.
4) J. Phillips, *Petroleum Refiner*, **38**, No. 9, 193 (1959).
5) E. Kuraku, S. Yagi and K. Negoro, *Science (Kagaku)*, **22**, 216 (1952).
6) E. Kuraku, S. Yagi and K. Negoro, ibid., **22**, 363 (1952).
7) K. Negoro, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **64**, 295 (1961),

spectrum of the benzene soluble fraction. After recrystallization of each fraction with ethyl alcohol, it was observed by the microscope that the adductible paraffin formed plate crystals, and the fractions soluble in pentane and benzene separated from micro-paraffin by chromatography also formed plate crystals. These phenomena were proved by the infrared spectra indicating that each fraction showed the characteristic crystal band[8] in the wavelength of 13.7~13.9 μ (wave number of 730~710 cm^{-1}).

On the contrary, the non-adductible paraffin showed a micro-crystalline state; the only exception was the pentane soluble fraction separated from non-adductible micro-paraffins by chromatography, which formed plate crystals.

Experimental

Formation of Urea Adducts.—Micro-paraffin was dissolved in benzene and treated with solid urea. The activators for the reaction were water and methyl alcohol. The formed molecular compounds of urea and straight chain paraffins (urea adducts) were separated from the non-adductible paraffin with urea by a suction filter with a vacuum pump.

The adducts were dried to constant weight watching the temperature to avoid decomposition, and finally, were decomposed with hot water. The adductible paraffins were separated from urea by dissolving them in hot water.

They were separated by filtration as they solidified with the drop of temperature. They were completely dried in a desiccator and weighed. The so-called urea reject or adductible paraffin, was weighed after benzene, methyl alcohol and water were expelled by solvent recovery apparatus. The conditions of the experiments are shown in Table I.

TABLE I. UREA ADDUCTS REACTION

Micro-paraffin	112.5 g.
Benzene	1700 cc.
Urea	450.0 g.
Methyl alcohol for activator	45 cc.
Water	4.5 cc.
Reaction temp.	33°C
Reaction time	50 min.
Drying temp. of adducts	35~45°C
Drying time of adducts	60 hr.
Hot water	6000 cc.
Temp. of hot water	70~80°C

The materials used in the experiment were as follows:

Methyl alcohol: b. p. 65°C, refined from commercial first grade product by distillation.

Benzene: b. p. 80°C, refined from commercial product by ordinary method[9].

Urea: m. p. 132.6°C, refined by recrystallization method.

Chromatography. — Each of the adductible and non-adductible paraffins was dissolved in a large quantity of pentane.

Twenty grams of the adductible paraffin was weighed out and dissolved in 16 l. of pentane; and 20 g. of the non-adductible paraffin was weighed out as above and dissolved in 12 l. of pentane.

Each of the two was charged into the column for chromatography, and treated with pentane, benzene, and ethyl alcohol to be separated into their soluble fractions.

The column used was a glass tube of 160 cm. in length and 6 cm. in diameter, and packed with 3 kg. of 80 mesh silica gel that had been dried for 8 hr. at 120°C.

Measurement of Physical Properties. — *Mean Molecular Weight.*—Measured by the depression of freezing point[10] in refined benzene.

Melting Point.—Measured by the method of dropping point[11].

Refractive Index.—Measured by an Abbe refractometer at 70°C (higher than melting point of paraffins).

Observation of Crystals[12].—The adductible and non-adductible paraffins and their pentane, benzene and ethyl alcohol soluble fractions separated by chromatography were recrystallized with solvent (ethyl alcohol; b. p. 78°C). The crystals were observed with ordinary or phase-contrast microscopes. One gram of each paraffin sample was dissolved in 300 cc. of ethyl alcohol and the solution was warmed to 70°C in a thermostat. Then, it was gradually cooled to room temperature and recrystallized.

Measurement of Ultraviolet Absorption Spectrum. — A photo-electric spectrophotometer of Type EPU-2 manufactured by Hitachi Mfg., Co. was used for the measurement of ultraviolet absorption spectrum. About 0.5 g. of the sample was taken and weighed accurately, and then dissolved in 5 g. of refined *n*-hexadecane to make up the solution of concentration of 10 wt. %. The solution was diluted to a tenth its former strength by the weighing method, successively, to make concentrations of 1, 0.1 and 0.01%. The ultravioled spectra of these solutions were measured at room temperature. *n*-Hexadecane, refined from commercial special grade product by the same process as the previous report[13], was confirmed to be fit for a diluent by measuring the degree of transparency in the range of wavelength of 220~420 mμ.

8) K. Negoro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 229 (1951)..

9) "Text-book of Chemical Experiment" (Jikken Kagaku Koza) 2 (Fundamental Technique II), Maruzen, Tokyo (1956), p. 73.

10) J. Sameshima, "Experimental Methods of Physical Chemistry" (Butsuri Kagaku Jikkenho), Shokabo, Tokyo (1941), p. 227.

11) Nippon Oil Co., "Test-methods of Petroleum" (Sekiyu Shikenho), Sekiyu-keizai-kenkyukai, Tokyo (1954), p. 218.

12) S. Yagi and K. Negoro, *Chem. Ind. Japan* (*Kagaku Kogyo*), **8**, 1112 (1957).

13) K. Negoro, *Report of Central Research Laboratory, Nippon Mining Co.* (*Nikko Chuo Shikenjo Shoho*), **11**, No. 3, 1139 (1960).

Measurement of Infrared Absorption Spectrum. — A infrared spectrophotometer of Perkin Elmer Model-21 was used for the measurement of infrared spectrum. The sample of the adductible or non-adductible paraffins and each fraction separated by chromatography were applied on the spectrophotometer and measured.

Results and Discussions

Results of Urea Adducts Formation. — The micro-paraffins which were obtained from the tank residues of Arabian crude oil were treated with urea, and the results are shown in Table II.

Table II. Urea treatment of micro-paraffin

Material	Weight, g.	Yield, %
Micro-paraffin	112.5	100.0
Urea adductible paraffin	69.5	61.8
Urea non-adductible paraffin	33.1	28.9
Loss	9.9	9.3

According to Philips[4], it was reported that micro-crystalline waxes contained 20~90% of urea adductible components. Turner et al.[14] reported that ordinary crystalline waxes contained 80~90% of *n*-paraffin by the results of the examination by mass-spectra on 16 sorts of paraffins. As results of the above reports, it is considered that the so-called micro-paraffins have higher molecular weight than that of the ordinary crystalline waxes and that the former contain side chain substances in a larger amount than the latter. It seems to be reasonable to consider that isoparaffins which have some side chains and the paraffins which have one or two aromatic or naphthene rings form adducts with urea as reported by Zimmerschied[15].

It will not be stated that all the components of such urea adductible paraffins consist of *n*-paraffin alone (small quantities of side-chain paraffins may be contained). The above consideration will also be confirmed by the results of chromatography, ultraviolet spectroscopy, and infrared spectroscopy as mentioned below.

Results of Chromatography and Properties of Each Fraction. — The adductible and non-adductible paraffins were separated by chromatography with silica gel.

The yields of each fraction are shown in Table III.

Great differences of the yields of each fraction were not seen between the two paraffins. However, there were great differences between the results of the physical properties of each fraction as shown in Table IV.

The non-adductible paraffins have higher mean molecular weights, lower melting points, and very much higher refractive indices than the adductible paraffins. Then, it was shown that in micro-paraffins, straight-chain hydrocarbons were separated effectively from substances having side-chains and aromatics.

Table III. Results of chromatography

	Micro-paraffin	Urea adductible paraffin	Urea non-adductible paraffin
Pentane soluble fraction	75.4 (76.8)*	79.0 (86.8)	76.5 (84.5)
Benzene soluble fraction	17.0 (17.3)	9.5 (10.4)	9.5 (10.5)
Ethyl alcohol soluble fraction	5.8 (5.9)	2.5 (2.8)	4.5 (5.0)
Loss	1.8 (—)	9.0 (—)	9.5 (—)
Total	100.0 (100.0)	100.0 (100.0)	100.0 (100.0)

* The values in ( ) show the yield (%) of each fraction, from which loss is subtracted.

Table IV. Physical properties of each fraction

	Mean molecular weight		M. p., °C		Refractive index, n_D^{70}	
	A Urea adductible paraffin	B Urea non-adductible paraffin	A	B	A	B
Base micro-paraffin	613	620	67.0	54.4	1.4400	1.4460
Pentane soluble fraction	607	636	65.0	54.0	1.4390	1.4410
Benzene soluble fraction	591	602	20	20	1.5050	1.5200
Alcohol soluble fraction	636	627	67.0*	46.5*	—**	—**

* Though each fraction was dropped at 57.0 or 46.5°C in measuring, some parts of the residues were solid. It was difficult to determine the melting point.

** Measurements were impossible.

14) W. R. Turner et al., *Ind. Eng. Chem.*, **47**, 1219 (1955).

15) W. J. Zimmerschied et al., ibid., **42**, 1300 (1950).

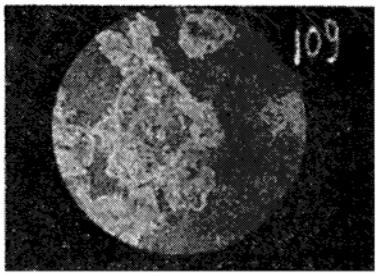

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Fig. 1. Urea adductible paraffin (A).

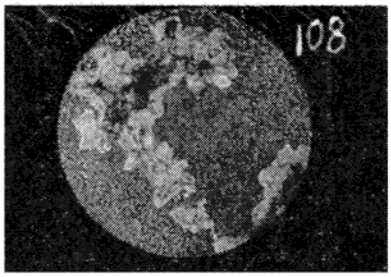

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Fig. 2. Urea non-adductible paraffin (B).

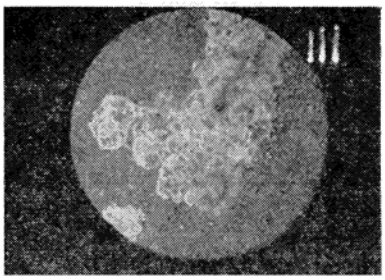

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Fig. 3. Pentane franction of A.

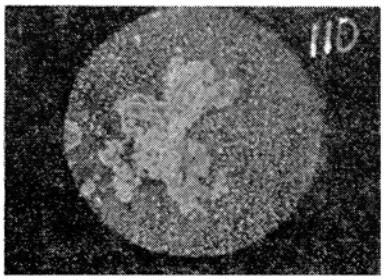

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Fig. 4. Pentane fraction of B.

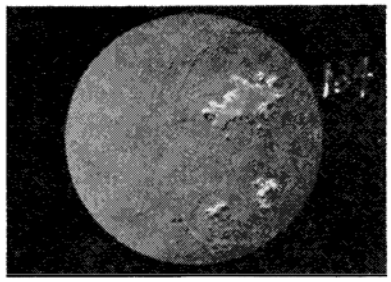

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Fig. 5. Benzene fraction of A.

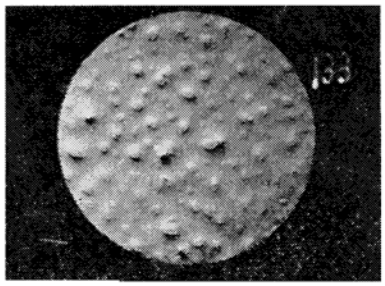

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Fig. 6. Benzene fraction of B.

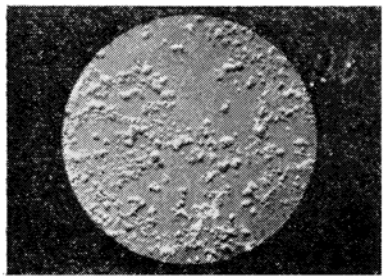

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Fig. 7. Alcohol fraction of A.

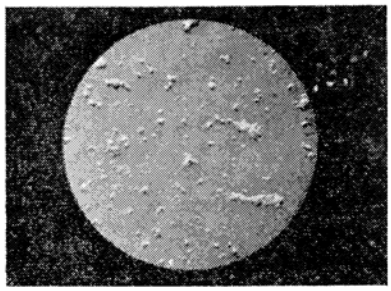

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Fig. 8. Alcohol fraction of B.

In particular, by the fact that the non-adductible paraffins have very high refractive indices, it should be suggested that they consist of complicated compounds[16].

It has already been known that hydrocarbons with side-chains and aromatic or naphtheric substances have lower melting points and higher refractive indices[17,18].

16) P. T. Edwards, *Petroleum Refiner*, **36**, 180 (1957).
17) A. N. Sachanen, "The Chemical Constituents of Petroleum", Reinhold Publ. Corp., New York (1945), pp. 289—296.
18) K. Negoro, *Chemistry (Kagaku)*, **15**, No. 5, 16 (1960).

Results of the Observation of Crystals.—Each fraction obtained by chromatography from the non-adductible paraffins was recrystallized with ethyl alcohol and observed through a microscope.

The results of the observation are shown in Figs. 1—8. Figure 1 shows the adductible paraffin which forms plate crystals smaller than those of the ordinary crystalline paraffin wax.

On the other hand, the non-adductible paraffin is in a very micro-crystalline state as shown in Fig. 2.

The growth of plate crystals of the pentane soluble fraction of urea adductible paraffin (Fig. 3) has progressed further than those of base paraffin, and the pentane soluble fraction of urea non-adductible paraffin (Fig. 4) also develops to plate crystals. The benzene soluble fraction of urea adductible paraffin from plate crystals as shown in Fig. 5, but that of urea non-adductible paraffin is microcrystalline as shown in Fig. 6. The ethyl alcohol soluble fractions of the two (adductible and non-adductible) were very fine and amorphous as shown in Figs. 7 and 8. These were very different from the other fractions.

The results of such observations through the microscope conformed to the results of measurement of infrared spectra of each paraffin, and these facts are interesting for the investigation on microcrystallization of micro-paraffin.

Results of Measurement of Ultraviolet Spectrum. — Each fraction of urea adductible or non-adductible paraffins was diluted with *n*-hexadecane, and its degree of transparency

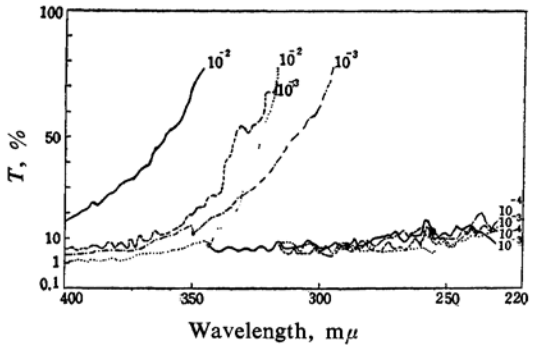

Fig. 9. Urea adductible paraffins.
——— Urea adductible paraffin (A)
------ Pentane fraction of A
—·—· Benzene fraction of A
····· Alcohol fraction of A

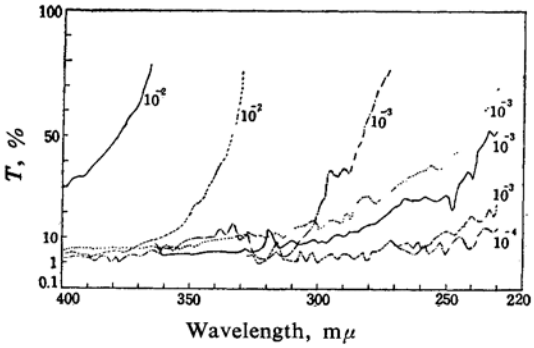

Fig. 10. Urea non-adductible paraffins.
——— Urea non-adductible paraffin (B)
------ Pentane fraction of B
—·—· Benzene fraction of B
····· Alcohol fraction of B

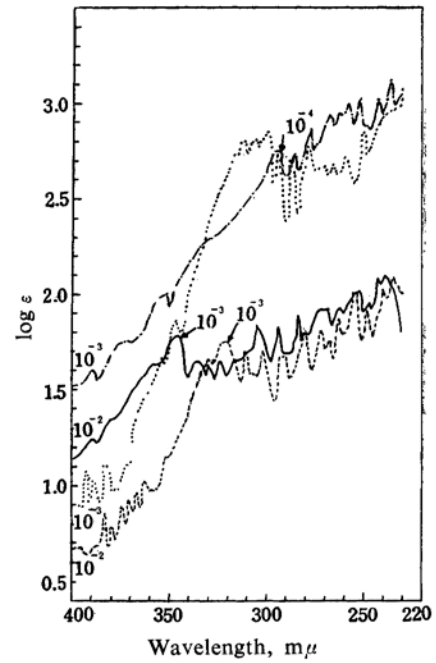

Fig. 11. Ultraviolet spectra of urea adductible paraffins.
——— Urea adductible paraffin (A)
------ Pentane fraction of A
—·—· Benzene fraction of A
····· Alcohol fraction of A

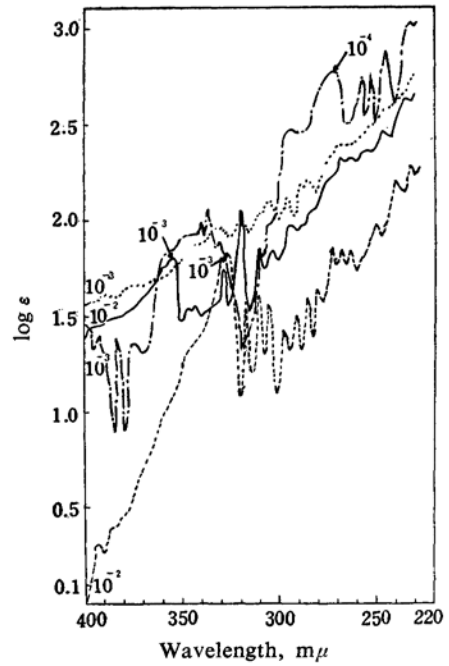

Fig. 12, Ultraviolet spectra of urea non-adductible paraffins.
——— Urea non-adductible paraffin (B)
------ Pentane fraction of B
—·—· Benzene fraction of B
····· Alcohol fraction of B

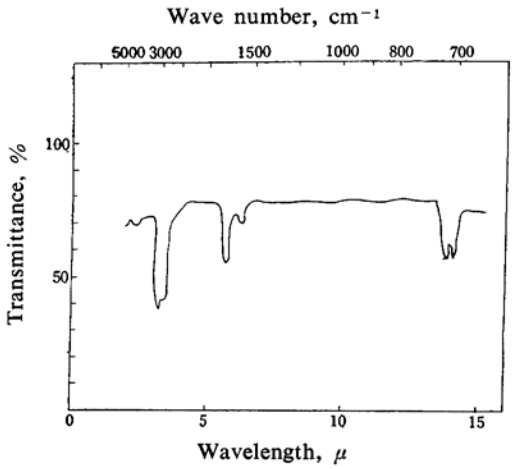

Fig. 13. Infrared spectrum of the urea adductible paraffins.

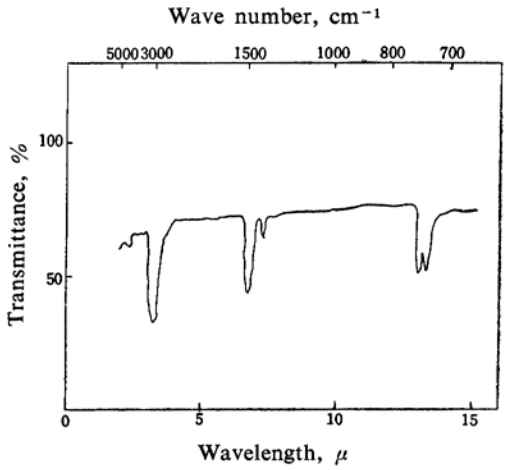

Fig. 14. Infrared spectrum of the pentane fraction of urea adductible paraffins.

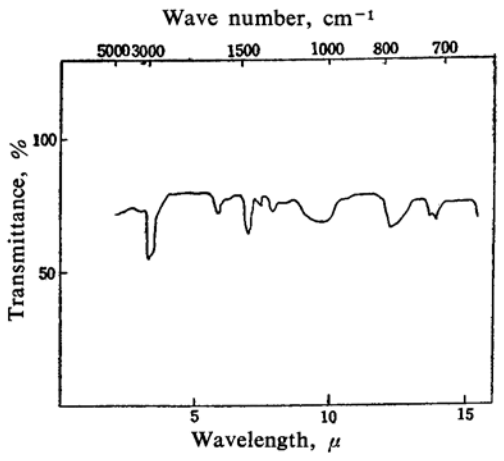

Fig. 15. Infrared spectrum of the benzene fraction of urea non-adductible paraffins.

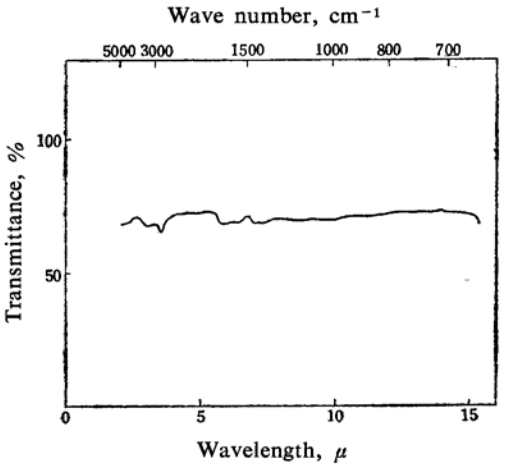

Fig. 16. Infrared spectrum of the alcohol fraction of urea adductible paraffins.

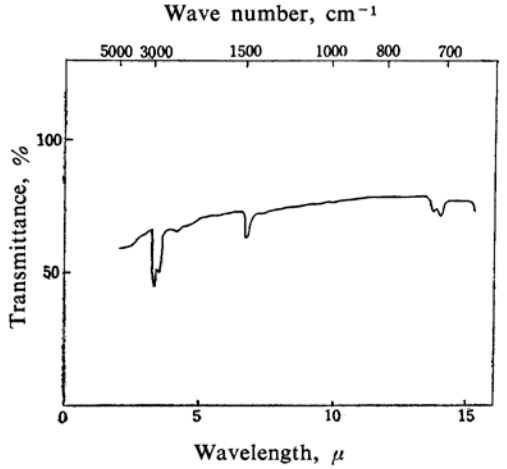

Fig. 17. Infrared spectrum of the urea non-adductible paraffins.

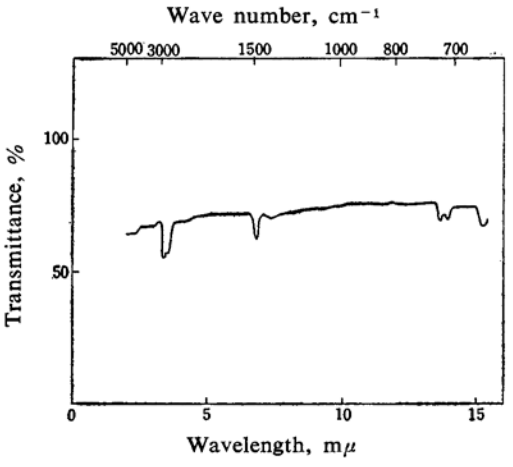

Fig. 18. Infrared spectrum of the pentane fraction of urea non-adductible paraffins.

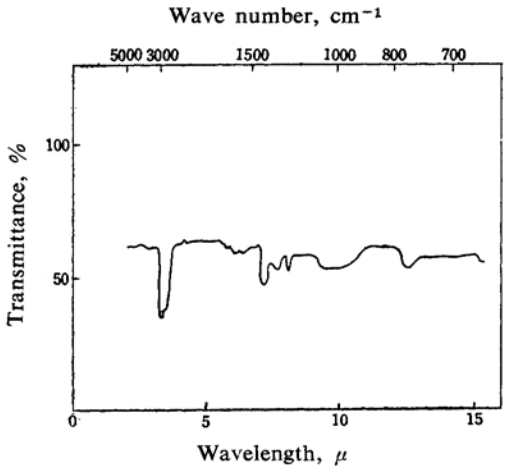

Fig. 19. Infrared spectrum of the benzene fraction of urea non-adductible paraffins.

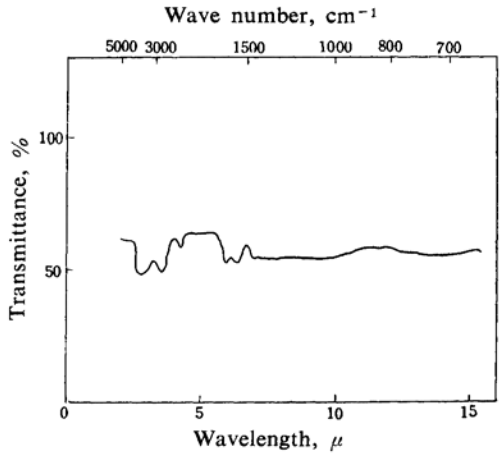

Fig. 20. Infrared spectrum of the alcohol fraction of urea non-adductible paraffins.

Tabble V. Infared spectrum of the urea adductible paraffin

Wavelength, μ	Wave number, cm⁻¹	Assignment of vibrations
3.35	2990	C-H (aliphatic) stretching vibration
3.43	2850	C-H (aliphatic) stretching vibration
6.85	1458	Deg-C-H bending vibration
7.29	1369	Syn-C-H bending vibration
13.83	723	Crystal band
14.04	712	Crystal band

Table VI. Infared spectrum of the pentane fraction of the urea adductible paraffin

Wavelength, μ	Wave number, cm⁻¹	Assignment of vibrations
3.37	2950	C-H (aliphatic) stretching vibration
3.44	2820	C-H (aliphatic) stretching vibration
6.84	1460	Deg-C-H bending vibration
7.27	1372	Syn-C-H bending vibration
13.82	723	Crystal band
14.02	713	Crystal band

Table VII. Infrared spectrum of the benzene fraction of the urea adductible paraffin

Wavelength, μ	Wave number, cm⁻¹	Assignment of vibrations
2.90	3450	O-H stretching vibration
3.37	2950	C-H (aliphatic) stretching vibration
3.40	2850	C-H (aliphatic) stretching vibration
5.85	1708	C=O stretching vibration
6.25	1597	Conjugated double bond stretching vibration ?
6.84	1460	Deg-C-H bending vibration
7.27	1373	Syn-C-H bending vibration
7.96	1254	Aromatic derivative vibration ?
12.62	792	
13.83	724	Crystal band
14.02	713	Crystal band

Table VIII. Infrared spectrum of thf alcohol fraction of the urea adductible paraffin

Wavelength, μ	Wave number, cm⁻¹	Assignment of vibrations
2.95	3390	O-H stretching vibration
3.40	2880	C-H (aliphatic) stretching vibration
5.83	1710	C=O stretching vibration

Table IX. Infrared spectrum of the urea non-adductible paraffin

Wavelength, μ	Wave number, cm^{-1}	Assignment of vibrations
3.36	2950	C-H (aliphatic) stretching vibration
3.44	2820	C-H (aliphatic) stretching vibration
4.00	2380	
6.83	1461	Deg-C-H bending vibration
13.84	723	Crystal band
14.03	713	Crystal band

Table X. Infrared spectrum of the pentane fraction of the urea non-adductible paraffin

Wavelength, μ	Wave number, cm^{-1}	Assignment of vibrations
3.36	2950	C-H (aliphatic) stretching vibration
3.44	2820	C-H (aliphatic) stretching vibration
6.85	1580	Deg-C-H bending vibration
7.31	1365	Syn-C-H bending vibration
13.85	722	Crystal band
14.04	712	Crystal band

Table XI. Infrared spectrum of the benzene fraction of the urea non-adductible paraffin

Wavelength, μ	Wave number, cm^{-1}	Assignment of vibrations
2.55	3930	
3.37	2950	C-H (aliphatic) stretching vibration
3.44	2820	C-H (aliphatic) stretching vibration
5.88	1700	C=O stretching vibration
5.99	1695	
6.27	1590	Conjugated double bond stretching vibration ?
6.87	1455	Deg-C-H bending vibration
7.29	1360	Syn-C-H bending vibration
7.97	1254	Aromatic derivatives vibration ?
12.55	797	
14.07	712	$-(CH_2)-$ rocking vibration

Table XII. Infrared spectrum of the alcohol fraction of the urea non-adductible paraffin

Wavelength, μ	Wave number, cm^{-1}	Assignment of vibrations
2.50	4000	
2.58	3880	
2.86	3500	O-H stretching vibration
3.37	2950	C-H (aliphatic) stretching vibration
3.44	2820	C-H (aliphatic) stretching vibration
4.20	2760	
5.82	1715	C=O stretching vibration
5.87	1700	
6.05	1650	
6.21	1610	Conjugated double bond stretching vibration ?
6.49	1540	
6.85	1458	
7.32	1358	

($T\%$) was measured; the results are shown in Figs. 9 and 10.

The ultraviolet spectra of the two paraffins are shown in Figs. 11 and 12, in which ordinate means $\log \varepsilon$ and abscissa wavelength ($m\mu$) calculated from the above results.

As [the results of such ultraviolet spectra, it is considered that both of the urea adductible and non-adductible paraffins contain various aromatics though their quantities are small.

Results of Measurement on Infrared Spectrum. —The results of the infrared spectra measured on each fraction of urea adductible and non-adductible paraffins are shown in Figs. 13—20. Though it is difficult to analyze any spectra on each fraction, the assignment of the main

vibrations has been considered as shown in Tables V—XII in reference to the results of Randall and others[19].

It was reported in our previous paper[7,8] that the results of the observation by microscope was noteworthy, showing that any substances in plate crystals had a crystal band in the range of wave number of 710~730 cm^{-1} (or wavelength of 13.7~13.9 μ).

Conclusion

Comparing the urea adductible with non-adductible paraffin, there have been considerable differences in each fraction. In particular, it is very interesting that the alcohol fraction has the spectrum assigned to O-H streching vibration, which has been suggested to be the cause of micro-crystallization. It is considered that the substances which are the cause of micro-crystallization shall be contained in the alcohol fraction of urea non-adductible paraffins.

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19) H. N. Randall et al., "Infra-red Determination of Organic Structure", O. van Nostrand Co., New York (1949).