Decomposition Temperature of Urea Adducts

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Decomposition temperatures for urea adducts of *n*-hexadecane, *n*-nonadecane, and *n*-paraffins from C_{19}–C_{20} fraction of mineral oil were determined. The results were compared with the data by Redlich et al.[1] and decomposition temperature of *n*-hexadecane by the author was found to be lower than that of Redlich's.

Addition of benzene to the system (adducts and water) results in the lowering of decomposition temperature. This effect becomes remarkable with a decreasing amount of water.

Experimental

Reagents.—Urea (m. p. 132.6°C) was recrystallized from aqueous solution saturated at 30°C. Methanol (b. p. 64~65°C), benzene (b. p. 80~80.5°C) and petroleum ether (b. p. 40~60°C) were redistilled from the commercial product.

n-Hexadecane (commercial) was treated with activated alumina followed by sulfuric acid and sulfur trioxide treatment, m. p. 16.2°C, $n_D^{20}=1.4251$.

n-Nonadecane and *n*-heneicosane were separated from lubricating oil fraction of Yabase crude (b.p. 104~226°C at 3 mmHg) by urea adduction and chemical treatment as mentioned above. Physical constants of these hydrocarbons were compared with the literature values[2,3] and shown in Table I.

Preparation of Adducts.—Adducts from mineral oil (Yabase lubricating oil fraction as described above) were prepared by adding 120 g of urea and 1 cc. of methanol to 150 g. of oil. After the mixed solution being stirred for 50 min., the adduct produced was filtered off and washed with 1500 cc. of benzene. Yield, 150 g. of adducts. Adducts of *n*-paraffins were made from the petroleum ether solution of them. This solution was treated with 3 times of urea to *n*-paraffins, and 0.3 times of methanol, and was stirred for 50 min. The adducts produced were filtered by suction and washed with 30 times the quantity of benzene.

All of these adducts were dried in vacuo until solvent odor was diminished. Analytical data are shown in Table II. Mole ratios in this table were determined by Schiessler's method[4]. Dissociation temperatures were measured by the method of Knight et al.[5]; according to the present author's experiment, dissociation temperatures of *n*-paraffins are quite similar to that of methyl ester which has been measured by Knight et al.

TABLE I. PHYSICAL CONSTANTS OF *n*-NONADECANE AND *n*-HENEICOSANE

Hydrocarbons	Refractive index (n_D^{60})		Melting point (°C)	
	Found	Lit.	Found	Lit.
n-Nonadecane	1.4268	1.4255	31.0	32.0
n-Heneicosane	1.4300	1.4290	40.5	40.5

Procedure.—A small test tube of 2.5 cm. diameter was connected in a large test tube of 4.5 cm. diameter with a rubber stopper. Two

1) O. Redlich, et al., *J. Am. Chem. Soc.*, **72**, 4153 (1950).
2) C. Kroeger and F. Hallfeld, *Erdöl u. Kohle*, **7**, 811 (1954).
3) M. F. Sawer et al., *J. Inst. Petrol.*, **27**, 1 (1941).
4) R. W. Schiessler and D. J. Flitter., *J. Am. Chem. Soc.*, **74**, 1720 (1952).
5) H. B. Knight et al., *Anal. Chem.*, **24**, 1331 (1951).

TABLE II. COMPOSITIONS AND DISSOCIATION TEMPERATURES OF ADDUCTS

Hydrocarbons in adducts	Urea/*n*-paraffin Wt. ratio	Urea/*n*-paraffin Mol. ratio	Dissociation temp. (°C)
Lub. oil paraffin	3.5	—	125
n-Hexadecane	3.1	11.7(12)[6]	112
n-Nonadecane	3.2	14.1(13.9)	129
n-Heneicosane	3.1	14.6(14.6)	129

grams of adduct samples and water were put into the small test tube with a thermometer and a stirrer made of iron wire.

The large test tube was placed in a 500 cc. beaker where warm water was filled in, and heated. Constant hand stirring was continued with temperature rise of about 5°C/min. until a paraffin portion was separated on the upper layer, and this point was considered as the decomposition temperature.

Results and Discussion

Decomposition Temperature.—Table III shows the decomposition temperature, the average value taken from the two measurements. Decomposition curve was made according to the method of Redlich et al., as shown in Fig. 1. These curves were extrapolated and the intersection with the saturation curve (dotted line) of urea in water were considered as the decomposition point.

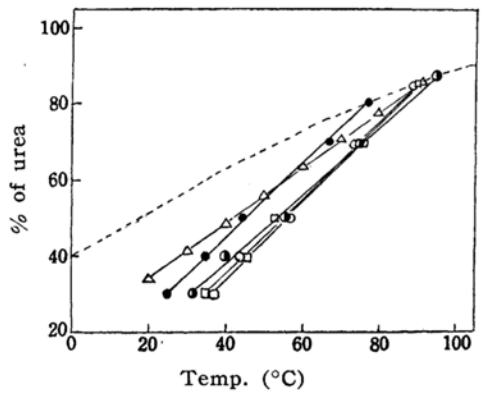

Fig. 1. Decomposition curve of urea adducts.
Dotted line: Urea saturation curve
◑: Mineral oil paraffin adducts
●: *n*-Hexadecane adducts
○: *n*-Nonadecane adducts
□: *n*-Heneicosane adducts
△: *n*-Hexadecane adducts by Redlich

As is shown in Table III, the decomposition point of *n*-hexadecane adduct is 78°C and is lowerthan Redlich's value, 90°C. Schlenk[7] showed that 97.5% of 1 mol. *n*-hexadecane adduct (12 mol. of urea and 1 mol. of *n*-hexadecane) was decomposed in 72 mol. of water at 31°C.

TABLE III. DECOMPOSITION TEMPERATURE OF UREA ADDUCTS

Hydrocarbons in adducts	Decomp. point (°C)	Urea[8] concn. (%)	Decomp. temp. (°C)
Lubricating oil paraffin	95	30	32.0
		40	39.5
		50	55.2
		70	75.0
n-Hexadecane	78	30	24.8
		40	35.0
		50	45.7
		70	67.0
n-Nonadecane	90	30	36.0
		40	43.5
		50	55.2
		70	74.5
n-Heneicosane	90	30	34.5
		40	44.0
		50	53.5
		70	75.0

This result means that 0.975 mol. of *n*-hexadecane adduct is decomposed 72 mol. of water at 31°C and 35.2% aqueous solution of urea is separated. According to the author's result, at the decomposition point of 31°C about 36% aqueous solution of urea is separated, and by Redlich et al. it corresponds to 41%. This deviation of the present result from the data of Redlich et al. was thought to be due to the difference of the determination method.

As *n*-nonadecane and *n*-heneicosane were separated from the same lubricating oil fraction, the decomposition points of these are nearly the same. *n*-Nonadecane sample used in this study is not so pure as is clearly seen from the comparison with the physical properties which have been cited in literature (cf. Table I), but in any case difference of the decomposition point between the carbon number ranges of 1 and 2 seemed to be comparatively small.

Effect of Benzene Addition.—The decomposition of adduct occurs when a sufficient amount of benzene or other hydrocarbon solvents were used at high temperatures. As might be expected, addition of benzene to the system which is composed of adduct and water, lowers the decomposition temperature. Fig. 2 shows the decomposition temperature of adducts containing

6) The values in the brackets were calculated by Redlich's equation[1], $m=0.653n+1.51$, where m is the mole ratio of urea to *n*-paraffin and n is the carbon number.

7) W. Schlenk. Jr., *Ann.*, **565**, 204 (1949).

8) Urea concentration means per cent of urea (in adducts) in the urea-water mixture.

43~233% (for urea in adducts) of water and 0~200% (for adducts) of benzene.

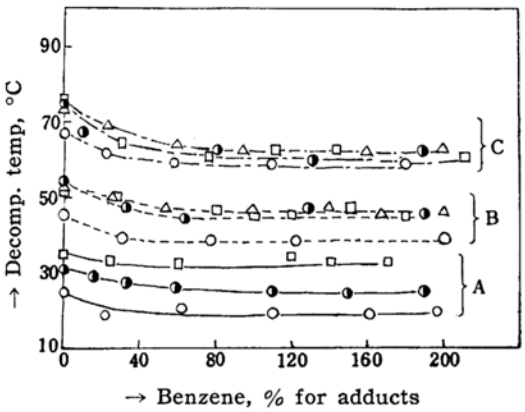

Fig. 2. Effect of benzene addition.
A: 233% water for urea in adducts,
B: 100%, C: 43%
◑: Mineral oil paraffin adducts
○: *n*-Hexadecane adducts
△: *n*-Nonadecane adducts
□: *n*-Heneicosane adducts

When the amount of benzene is increased, the decomposition temperature lowers; but the more the amount of water, the smaller the effect of benzene. The effect of benzene addition of 40~200% for adducts shows almost constant change of decomposition temperature: i. e., on addition of 233% water, temperature change is about 3~5°C, 100% water, 5~8°C, and 43% water, 10~12°C. This unchangeability of the decomposition temperature by the benzene addition may be caused by the limitation of decomposition by benzene itself. Hence, it can be seen that water has greater decomposition velocity than benzene has, and temperature dependence of the benzene decomposition is greater than that of water (Table IV).

Table IV shows the decomposition temperature of *n*-hexadecane adduct by benzene, and complete decomposition is obtained only when the boiling benzene (80°C) is used as 200% for adducts and five hours heating[9].

TABLE IV. DECOMPOSITION OF *n*-HEXADECANE ADDUCT BY BENZENE

Temp. (°C)	Heating time (hr.)	Benzene (% for adduct)	*n*-Hexadecane decomposed (%)
30	4	150	5
50	3	150	19
70	3	150	84
70	6	150	90
80	4	150	93
80	5	150	97.2
30	5	200	7
70	3	200	96
70	5	200	98.7
80	4	200	95
80	5	200	100

Decomposition temperatures of adducts of lower carbon paraffins are lower than those of higher ones, as might be expected from Fig. 2, yet this effect is less striking than water decomposition (Fig. 1).

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9) This decomposition is carried out without stirring.