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Thermal Study on Adducts of Urea with *n*-Alkanes and *n*-1-Alkanols

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Synopsis

Crystalline adducts of urea with *n*-alkanes (C_8～C_{20}) and *n*-1-alkanols (C_{12}～C_{18}) were prepared. From thermal analysis and X-ray diffraction study on the adducts, we found that the composition of adducts and the heat of decomposition can be obtained easily from the thermogram of adducts.

§ 1. Introduction

Since urea adducts were first discovered by Bengen[1)], many investigations[2)] on the characteristic property and structure have been carried out, due to the fundamental interests and the utility for the separation of hydrocarbons and their derivatives. All urea adducts are characterized by the same crystal lattice ; urea molecules (host molecules) form hexagonal pipes in which the organic molecules (guest molecules) are included. Generally, it is required that the guest molecules in the formation of the adducts are long and unbranched, since with most branched and cyclic hydrocarbons and their derivatives, the adducts are not formed[3)].

In this study, the adducts on urea with *n*-alkanes and *n*-1-alkanols were prepared from the saturated solutions of urea in methanol and examined by X-ray diffraction and thermal analysis. From these measurements, we established the method to determine the composition of urea and to measure the heat of decomposition.

§ 2. Experimental

Materials and Solvents

Urea as host molecule, *n*-alkanes (C_8～C_{20}) and *n*-1-alkanols (C_{12}～C_{18}) as guest molecules and methanol as solvent were used in this study and were reagent grade.

Crystallization Procedure

a. Adducts with *n*-alkanes

We prepared the saturated solutions of urea in methanol at room temperature, and a slight excess amount of *n*-alkane required for the formation of the adducts was added. In the case of solid *n*-alkanes, guest agents solved with several drops of hot benzene were added. The whole was stirred and immediately needlelike crystals precipitated out. They were collected on glass filters and washed with n-pentane and then dried.

b. Adducts with *n*-1-alkanols

A slight excess of *n*-1-alkanol required for the formation of the adducts, was added to the saturated solutions of urea in methanol at 40°C. In the case of solid *n*-1-alkanol, guest agents was added to the solutions at 60°C. The solution was stirred and then cooled to room temperature to obtain the crystalline precipitates of the adducts.

X-Ray Diffraction Study

X-ray powder patterns were obtained by a diffractometer by use of CuK_α radiation. The precipitates of urea-*n*-alkanes and urea-*n*-1-alkanols gave the same diffraction patterns as those already shown by other investigators[4)5)].

Thermal Analysis

A Perkin-Elmer Differential Scanning Calorimeter (D. S. C.) was used for the thermal analysis. The temperature scale was calibrated by the onset of the melting of Indium at 429°K, heated at the same rate as that in the sample.

§ 3. Results and Discussion

Thermogram at the heating rate of 10°C/min. for the adduct of urea with eicosane (n-$C_{20}H_{42}$) is shown in Figure 1. The thermogram has two dististinct endothermic peaks in which the higher temperature peak agrees with the melting temperature (133°C) of pure urea, and the lower temperature peak is considerably higher than the melting temperature (36.4°C) of pure eicosane and is lower than it's vaporization temperature. The lower temperature peak may correspond to the decomposition of adduct. In Figure 2, we show the X-ray diffraction patterns for the adduct of urea with eicosane annealed at the temperatures above and below the lower temperature peak (125°C). As shown in Figure 2, the X-ray diffraction pattern of the specimen annealed at 115°C for 30 min. is the same pattern as that of the original specimen. However, annealing of the adduct at 129°C for 30 min. results in a new diffraction pattern which agrees with that of pure urea. Thus we shall conclude that the lower temperature endothermic peak in the thermogram of Figure 1 means the decomposition of the adduct accompaning with the transition of crystalline urea from hexagonal to tetragonal and the higher peak means the fusion of the tetragonal urea crystals.

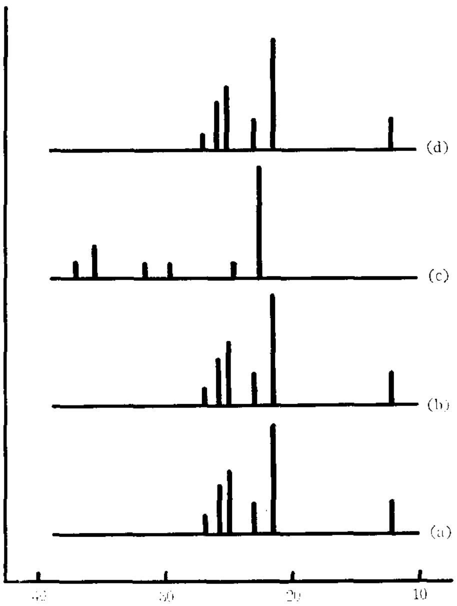

Fig. 2 X-ray powder patterns of the adduct of urea with eicosane. (a) original specimen, (b) annealed at 115°C, (c) annealed at 129°C and (d) specimen (c) kept for 24 hrs at room temperature.

We can obtain the similar thermograms for the adducts of urea with other n-alkanes and n-1-alkanols as in Figure 1. Figures 3 and 4 show eight thermograms in which the higher temperature endothermic peaks are at constant temperature, but the temperature of the lower peaks reflects the stability of the adducts. The

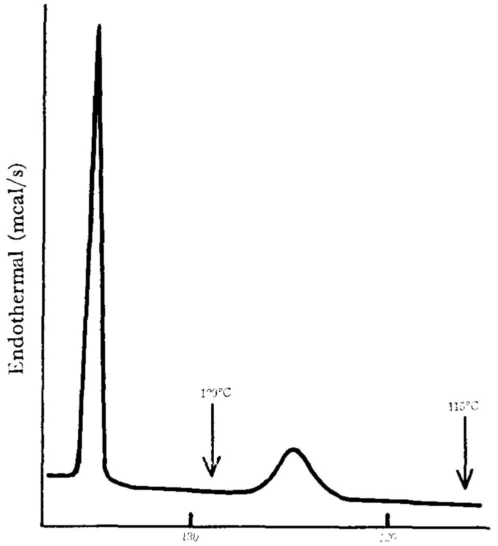

Fig. 1 D. S. C. thermogram of the adduct of urea with eicosane.

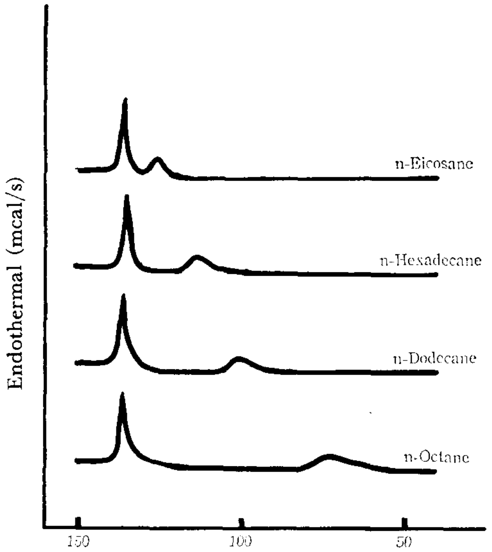

Fig. 3 D. S. C. thermograms of the adducts of urea with n-alkanes.

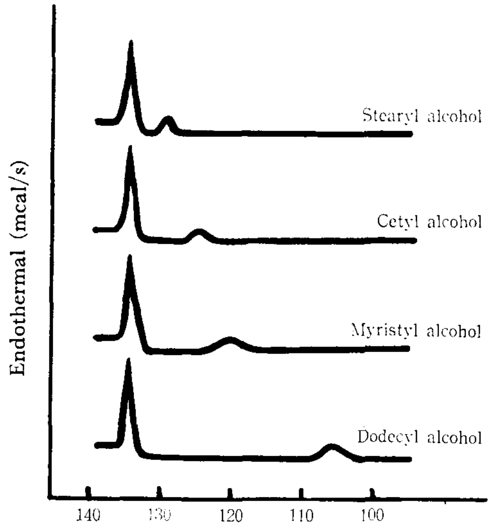

Fig. 4 D. S. C. thermograms of the adducts of urea with *n*-1-alkanols.

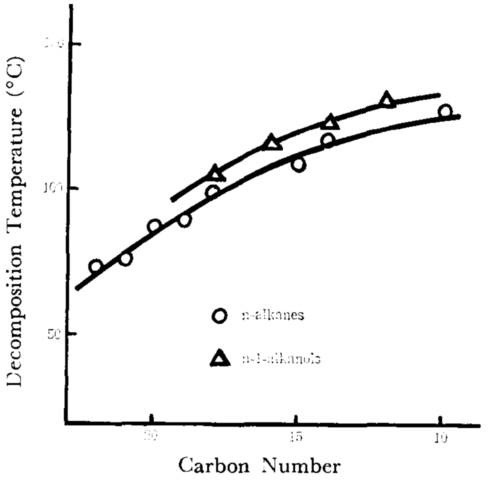

Fig. 5 Decomposition temperature of the adducts of urea with *n*-alkanes and *n*-1-alkanols vs carbon number of guest molecules.

relation between the stability (the temperatures of lower peaks of thermograms) of the adducts and chain length (carbon numbers) of guest molecules is shown in Figure 5. The stability of the adducts increases with chain length of guest molecules. All adducts in this study decompose by annealing at the temperature above the lower temperature endothermic peak and are stable for heating at the temperature below the lower peak. This was examined by X-ray diffraction.

Now, we can obtain the mole ratio of urea/guest and the heat of adduct formation by the following method. Firstly, the standard area A_0 under the endothermic peak of pure urea of W_0 (g) are measured. Secondly, the area A_1 under the higher temperature peak and A_2 under the lower temperature peak are measured. So the mass of urea in the adduct is represented by $(A_1/A_0) \times W_0$ (g) and the mass of the guest molecule is also represented by subtracting this value from the whole weight of the adduct. Thus, the heat of adduct formation can be represented by $(A_2/A_0) \times (60W_0)$ (cal/mole-guest), using the heat of fusion of pure urea 60 (cal/g).

In Figure 6 are shown the mole ratios against the carbon number of the guest molecules in the adducts. For *n*-alkanes, the relation between the mole ratio *m* and the carbon number *n* is given by,

$$m = 0.69n + 1.50 \qquad (1)$$

The slmilar result have already been presented by Smith[7]. Similarly, for *n*-1-alkanols, we obtained,

$$m = 0.69n + 0.50 \qquad (2)$$

Vertical distance between two lines represents the difference in the effect of chain ends, CH_3 and OH, that is, alkanols in the channel

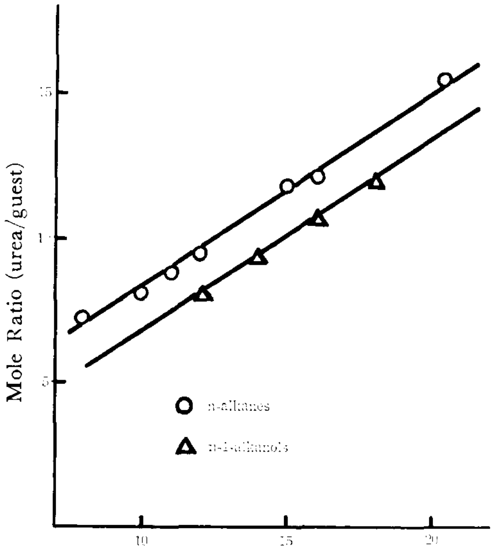

Fig. 6 Mole ratio of urea/guest for the adducts of urea vs carbon number of guest molecules.

of urea pack more compactly than the corresponding alkanes in carbon number.

In Figure 7 are shown the heat of decomposition of the adducts with *n*-alkanes measured in our experiment and the heat of formation already represented by Zimmershied and coworkers[2]. Thermodynamically, in the absolute value, the heat of formation of adduct must agree with the heat of decomposition of adduct. However, two lines are parallel and the values in our data lower by about 10% than those in their data. The reason why there are differences between the heat of formation and the heat of decomposition is not clear in present. Therefore, further examinations are required.

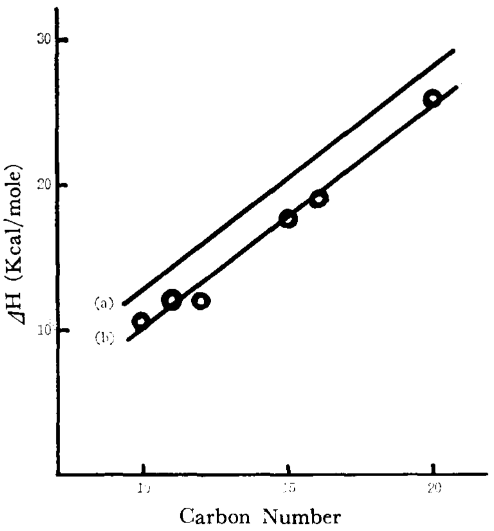

Fig. 7 The heat of formation and the heat of decomposition. The heat of formation (a) (Zimmershied's data) and the heat of decomposition (b) (our data) vs carbon number of guest molecules.

References

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4) Hendricks : J. Am. Chem. Soc., **50** (1928), 2455.
5) A. E. Smith : Acta. Cryst., **5** (1952), 224.