Heat of Solution of Methanolized Cellulose*

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In our previous papers[1,2], the lateral order distribution of cellulose was determined and discussed. In our laboratory the lateral order distribution has been determined from the solubility data of methanolized cellulose in aqueous sodium hydroxide solution of various concentrations.

Recently it has been shown that the solubility of methanolized cellulose depends on the degree of polymerization of the methanolized cellulose and that distribution obtained by such a method gives rather a longitudinal order distribution of crystallites. On the other hand, it has been shown that the effect of the degree of polymerization of hydrolyzed cellulose on its solubility is smaller than that of the lateral order[3].

The present investigation of heat of solution of methanolized cellulose was undertaken to obtain some informations

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[1] Y. Tsuda and S. Mukoyama, This Bulletin, **29**, 748 (1956).

[2] Y. Tsuda and S. Mukoyama, *Textile Research J.*, **27**, 945 (1957).

[3] H. Sobue, S. Fukuhara and M. Moriya, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 1015 (1958).

about the dependency of the solubility of methanolized cellulose on the cohesive energy of crystallites.

Experimental

Cellulose Samples. — Cuprammonium rayon, Shin-toramomen, BX-yarn[4], viscose rayon, tire-cord rayon A (conventional) and tire-cord rayon B (all-skin type) were used.

Methanolysis. — Methanolysis of the samples was performed at 40° for 24 hours with 1 N hydrogen chloride in absolute methyl alcohol. After methanolysis, the residue was filtered, washed with methanol until it became chloride-free and then dried.

Measurement of Heat of Solution. — The apparatus was a simple non-adiabatic calorimeter composed of a 100 ml. pyrex vacuum bottle, a Beckmann thermometer (in 0.01° division), a stirring rod and a sample inlet tube, as shown in Fig. 1.

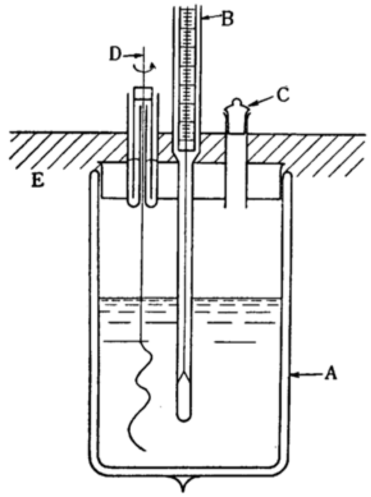

Fig. 1. Calorimeter.
A, 100 ml. pyrex vacuum bottle
B, Beckmann thermometer
C, Sample inlet tube
D, Stirrer
E, Thermostat

The apparatus was immersed in a thermostat kept at 20°. Methanolized sample (50 mg.) was bone-dried and kept at 20°. The solvent was 50 ml. of 11% aqueous sodium hydroxide solution, which was kept at 20° in the calorimeter. The stirring was done at a constant speed because constancy of the mechanical generation of heat was necessary for the measurement of small heat change. Under these experimental conditions observed temperature rise was about 0.05°, which was estimated to 0.001°. The dissolution of methanolized cellulose in the alkaline solution was a relatively rapid reaction. The heat capacity of calorimeter was determined experimentally under working conditions by measuring the heat of solution of potassium chloride in water.

Degree of polymerization was measured using cuprammonium solvent. Lateral order distribution was obtained by the same method as described in a previous paper[2].

Results

In Table I are shown the values of the heat of solution together with the statistical quantities which indicate their reliability. Degree of polymerization of methanolized cellulose is also shown in Table I. It is evident from Table I that the heats of solution of samples I, II and III are smaller than the others and those of samples V and VI are larger than the rest. The lateral order distribution of these samples is shown in Fig. 2.

TABLE I
HEAT OF SOLUTION

Methanolized	Heat of solution cal./g.	95% Confidence limit	Degree of polymerization
I Cuprammonium Rayon	27.6	±1.3	50
II Shin-toramomen	27.8	±1.2	45
III BX-yarn	29.2	±1.3	40
IV Viscose Rayon	31.4	±1.2	33
V Tire-cord Rayon A	33.4	±1.3	28
VI Tire-cord Rayon B	34.3	±1.1	25

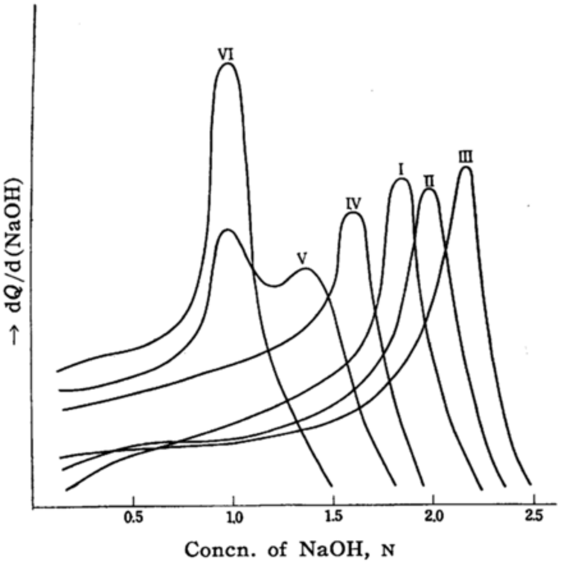

Fig. 2. Lateral order distribution (types identified in Table I).

Discussion

The heat of solution of the cellulose sample, H_s, can be separated in two parts as follows;

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[4] N. Drisch and L. Soep, *Textile Research J.*, **23**, 513 (1953).

$$H_s = H_a - E_c$$

where H_a is the heat of solution of amorphous cellulose in the alkaline solvent and E_c is the cohesive energy of the cellulose sample. H_a is a constant value with respect to all cellulose samples under a given experimental condition. Therefore the difference in the heat of solution of two samples can be regarded as the difference in their cohesive energies; that is, the larger the heat of solution, the smaller the cohesive energy. It will be seen from the results in Table I that the methanolysis residue of Shin-toramomen, Bx-yarn and cuprammonium rayon have large cohesive energy values and tire-cord rayons have rather low values. On the other hand, as shown in Fig. 2, the former shows high lateral order distributions and the latter shows low lateral order distributions. These relationships indicate that the distribution obtained from the fractional dissolution of methanolized cellulose corresponds to the distribution of cohesive energy. Although the degree of polymerization can be regarded as another factor of the fractional dissolution, its effect would be relatively small in comparison with the effect of cohesive energy.

It may be accepted from these relationships that the length of crystallite depends on the lateral order of crystallite and a portion of high lateral order can form a long crystallite, and therefore the dependency of lateral order distribution on the degree of polymerization has been observed.

If it is assumed that methanolysis destroys only the aggregated portion of very low cohesive energy, the cohesive energy of the methanolysis residue would be almost identical with that of the original cellulose.

Summary

The heat of solution of methanolysis residue of cellulose fibers was measured and then the difference in the cohesive energy of different samples was estimated. It was elucidated that the cohesive energy of methanolized cellulose corresponds to the experimentally evaluated lateral order.

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