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Resistance of *Valonia* Cellulose to Mercerization

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Synopsis

The mercerization behavior at 20°C. of *Valonia macrophysa* cellulose of Japanese origin was investigated by x-ray, moisture regain, and infrared spectrographic methods. The NaOH concentration range necessary for mercerization was 16–20%, which is higher than those required for wood pulp (8–11%), ramie or cotton (11–14%), and even the animal cellulose, Tunicin (14–16%). Treatment with the alkaline solution of the ordinary concentration (17.5%) for 4 days could not mercerize it, and even mercerization with a 19% solution brought about the presence of the reflection from $(101)_{II}$ along with those from $(101)_{I}$ and $(10\bar{1})_{I}$ after regeneration. Such a high resistance to mercerization of the *Valonia* cellulose may be due to its larger crystallite size rather than the crystalline content.

INTRODUCTION

It has long been known that cellulose I is mercerized with a 13–15% NaOH solution at 20°C. and converted to cellulose II after regeneration, but detailed investigations have shown that the alkaline concentration necessary for mercerization varies, depending on the origin of the cellulose. Rånby[1] reported that the necessary concentration at 0°C. is 5–7.5% for wood pulp and straw pulp, 7–9.5% for cotton and ramie, and 9–11% for the animal cellulose, Tunicin. According to Tsuda,[2] the values are 8–11% and 11–16% for wood pulp and linter pulp, respectively, at 20°C. Yurugi[3] and McKenzie and Higgins[4] also obtained similar results but with different methods of investigation.

The present authors found that the *Valonia* cellulose did not change to cellulose II after treatment with a 17.5% NaOH solution at 20°C. for as long as 4 days; indeed, 14 days were necessary for mercerization under these conditions. The animal cellulose, Tunicin, has been the only one which has a higher resistance to mercerization than ramie or cotton, so the mercerization behavior of this newly found sample is described in detail in the present report.

EXPERIMENTAL

Sample

A sample of *Valonia macrophysa* of Japanese origin collected at the seaside of the Izu peninsula was used. It was purified by boiling with a 1%

NaOH solution after Liang.[5] During the operation the *Valonia* cell wall was separated into a number of thin layers, 2–5 μ in thickness.

A sample of ramie was also purified in the same way.

Mercerization

The purified and dried sample was mercerized by immersion in an alkaline solution of various concentrations at 20°C. for 1 hr., followed by washing with water free of alkali and air-drying.

Heat Treatment

A part of the sample was heated at 170 or 190°C. for 10 min. in a sealed tube which contained a small quantity of water, just sufficient to wet the sample.

X-Ray Studies

Preliminary x-ray data showed that our sample has a selective uniplanar orientation and that the (101) plane lies parallel to the surface of the cell wall as well known on *Valonia ventricosa*.[6] The untreated or treated sample was cut into fine pieces, randomized, formed into a disk, 2 mm. in diameter, 1 mm. thick, and 7 mg. in weight, and used as specimen.

The x-ray apparatus used was a Geigerflex instrument (Rigaku Denki Ltd., Japan); conditions were 35 kv., 15 ma., with Ni-filtered CuKα radiation.

Infrared Spectra

A thin layer of *Valonia* film, 2–5 μ in thickness, was studied with an EPI-II apparatus doublebeam-type, constructed by Hitachi Ltd.

Moisture Regain

The moisture regain of the samples was measured after conditioning at 58% R.H. for 72 hr. at 20°C.

RESULTS

X-Ray Investigation

Figures 1 and 2 show the radial scanning curves of the *Valonia* and the ramie treated at 20°C. with the caustic alkaline solutions of various concentrations. The treatment with 11% solution converted the ramie cellulose I into cellulose II in accordance with the literature data, but in the case of the *Valonia*, treatment with a 17.5% solution for even 4 days could not mercerize it; treatment with a 19% solution produced the reflection from $(101)_{II}$, but this was present along with those from $(101)_I$ and $(10\bar{1})_I$.

The mercerization became less complete and more difficult when the *Valonia* had been heat-treated at 170 or 190°C. (omitted from the figure)

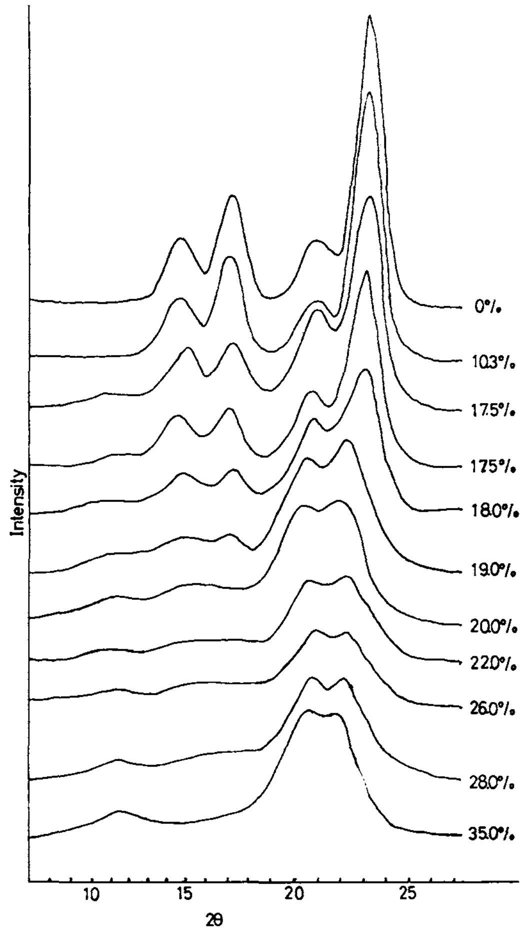

Fig. 1. Radial scanning curves of randomized *Valonia macrophysa* cell wall, treated with aqueous NaOH of various concentrations at 20°C. for 1 hr. except for (*4*), which was treated for 4 days. The curves are shifted vertically.

as can be seen in Figure 3, probably because of the annealing effect at such high temperatures in the presence of water.

Moisture Regain

The moisture regains of the *Valonia* and ramie samples above are indicated in Figure 4 in relation to the alkaline concentration used for the treatment. The untreated and the heat-treated *Valonia* could not be mercerized completely by dilute solutions (less than 20–21 and 22–24%, respectively), while the ramie was mercerized completely with a 16–17% solution as usual. This behavior is in accordance with the results of the x-ray investigation described in the preceding section.

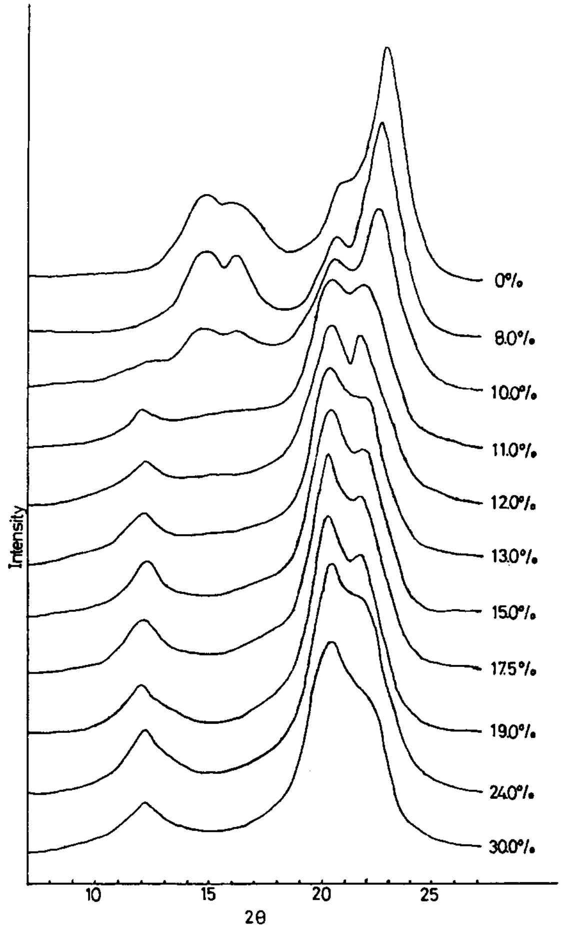

Fig. 2. Radial scanning curves of the ramie, treated with aqueous NaOH solutions of various concentrations at 20°C. for 1 hr. The curves are shifted vertically.

The moisture regain of the untreated *Valonia* is about 2–3% lower than that of the ramie. This is evidence for the decreased accessibility, i.e., higher crystallinity and larger crystallites, of the *Valonia* cellulose.

Infrared Spectrographic Investigation

The change in the infrared spectrogram in reference to the cellulose crystallinity has been studied by various authors: O'Connor[7] found that the optical density of the 1430 cm.$^{-1}$ band decreases and that of the 892 cm.$^{-1}$ (cellulose I) or 895 cm.$^{-1}$ (cellulose II) band increases as the crystallinity decreases, and they proposed the optical density ratio, D_{1430}/D_{892} as a measure of the crystallinity; this was considered, however, by Hurtubise and Krässig[8] as a lateral order index. McKenzie and Higgins[4] considered the 1430 cm.$^{-1}$ and 892 cm.$^{-1}$ bands to relate to cellulose I and

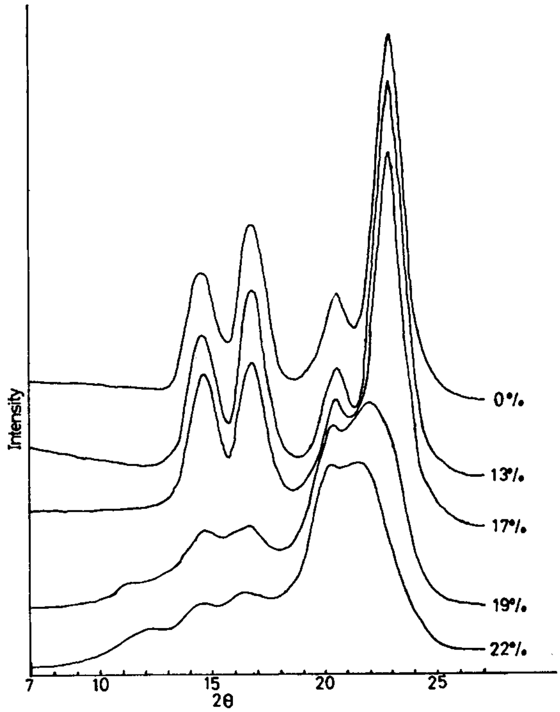

Fig. 3. Radial scanning curves of the *Valonia macrophysa* cell wall, heated at 170°C. for 10 min., followed by the alkaline treatment. The curves are shifted vertically.

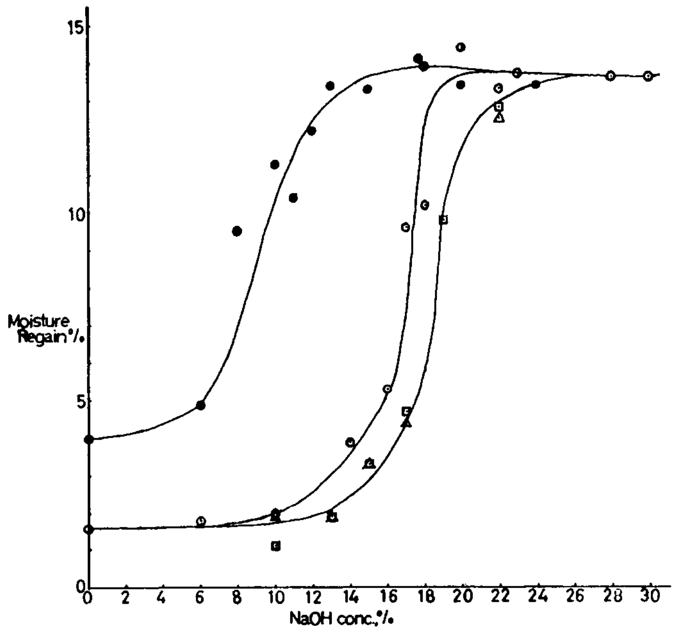

Fig. 4. Relation between the moisture regain and the concentration of NaOH used for the treatment: (●) ramie, (⊙) *Valonia*, untreated; (⊡) *Valonia*, heat-treated at 170°C. for 10 min., (△) Valonia, heat-treated at 190°C. for 10 min.

cellulose II, respectively, and they investigated the conversion of the lattice during the mercerization through these parameters.

In the present investigation, D_{1430}/D_{2908} decreases and D_{892}/D_{2908} increases as the mercerization proceeds, as indicated in Figures 5 and 6, in which the McKenzie-Higgins' data on wood pulp and cotton are included

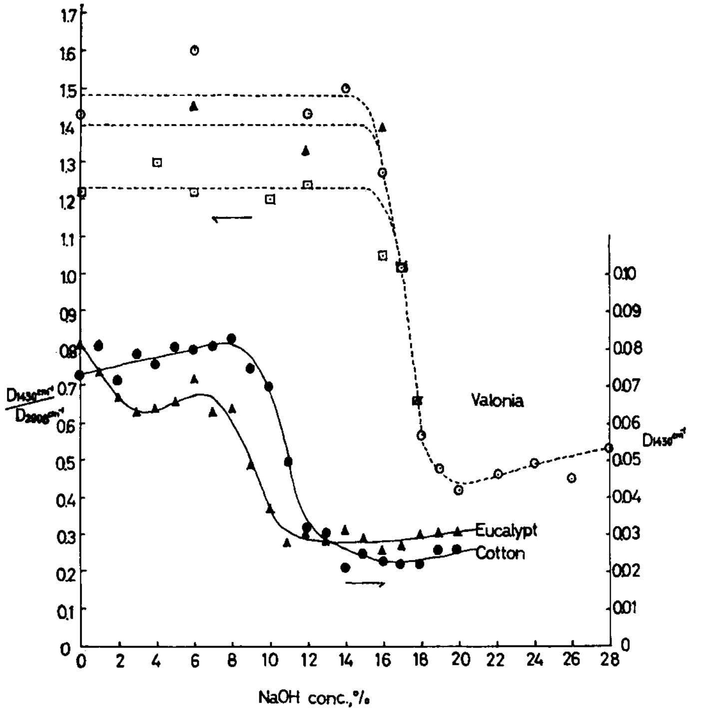

Fig. 5. Optical density at 1430 cm.$^{-1}$ vs. NaOH concentration. The curves of Eucalypt and cotton are reproduced from McKenzie and Higgins.[4]

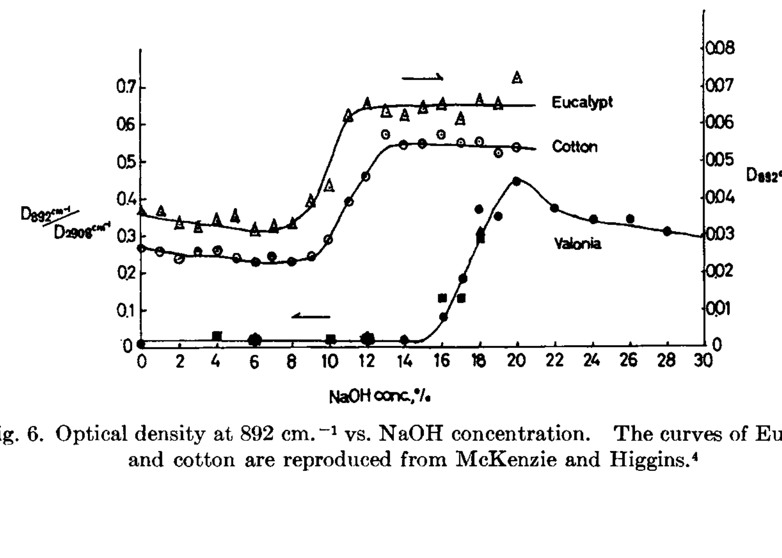

Fig. 6. Optical density at 892 cm.$^{-1}$ vs. NaOH concentration. The curves of Eucalypt and cotton are reproduced from McKenzie and Higgins.[4]

for the sake of comparison. These curves are of similar type, but the alkaline concentration necessary for the phase transition shifts to higher value in the order from the wood pulp (Eucalypt) to the *Valonia* through the cotton. They correspond well to the changes described in the preceding sections, but it is noteworthy that the parameter in the premercerization range is lowered by heat treatment. This will be the subject of a future study.

SUMMARY AND DISCUSSION

The alkaline concentration range necessary for the phase transition due to mercerization observed by the various methods in the present work along with those by the other authors on ramie or cotton at 20°C. are summarized in Figure 7. Of course, the sensitivity differs according to the methods used, so the ranges that bring about the outstanding change were employed there.

We can see that ramie and cotton are mercerized by a 10–14% solution, while the *Valonia* requires a 16–20% solution; this concentration range is clearly higher than that required for mercerization of ramie or cotton. Rånby has shown that a higher concentration (9–11% at 0°C.) is necessary for animal cellulose than that for cotton and ramie, (7–9.5%). According to Sobue and Hess,[9] who studied the effect of temperature on the concentration of mercerizing lye, the necessary concentration for the formation of soda cellulose I must be 4–5% higher at 20°C. than at 0°C.; then the concentrations necessary for the mercerization of cotton or ramie and animal cellulose at 20°C. are estimated, from the Rånby's data, to be 11–14% and 14–16%, respectively. The former concentration range coincides with our data, while the latter seems to be slightly lower for the *Valonia*.

As a result, a new cellulosic material with resistance to mercerization higher than that of Tunicin was found. This high resistance of *Valonia*

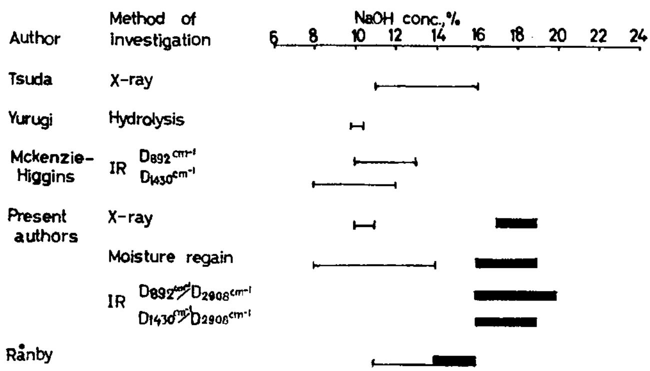

Fig. 7. Comparison of the NaOH concentration necessary for the mercerization at 20°C. obtained by the various authors. (——) ramie and cotton, (▬▬) *Valonia* and Tunicin. Rånby's value is estimated from his experiment at 0°C.

cellulose is in agreement with the view of Preston,[10] who pointed out the larger crystallites of *Valonia* cellulose.

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Résumé

On a étudié la mercérisation de comportement à la mercérisation à 20°C de la cellulose de *Valonia Macrophysa* d'origine Japonaise et utilisant les rayons-X, le regain de l'humidité et les méthodes spectrographiques infrarouges. La concentration en soude caustique nécéssaire pour mercériser cette cellule, de 16–20%, était plus élevée que celle requise pour la pulpe de bois (8–11%), la ramie ou le coton (11–14%) et même pour la cellulose animale, la Tunicine (14–16%). Le traitement avec une solution alcaline de concentration ordinaire, 17.5%, durant 4 jours ne permettait pas la mercérisation et même la mercérisation avec une solution à 19% présentait la réflection au départ de $(101)_{II}$ avec $(101)_I$ et $(10\bar{1})_I$ après régénration. Cette haute résistance à la mercérisation de la cellulose *Valonia* pourrait être due à la grandeur plus élevée des cristallites plutôt qu'à la teneur en fraction cristalline.

Zusammenfassung

Das Mercerisierungsverhalten von *Valonia-Macrophysa*-Cellulose japanischen Ursprungs bei 20°C wurde mit Röntgen-, Feuchtigkeitsaufnahme-und IR-Methoden untersucht. Die zur Mercerisierung notwendige NaOH Konzentration lag im Bereich 16–20% und war damit höher als die für Holzpulp (8–11%), Ramie oder Baumwolle (11–14%) und sogar für die tierische Cellulose Tunicin (14–16%) erforderliche. Die Behandlung mit einer alkalischen Lösung der üblichen Konzentration, 17,5%, durch 4 Tage führte nicht zur Mercerisierung und die Mercerisierung mit einer 19% Lösung ergab nach Regenerierung die Reflexion von $(101)_{II}$ zusammen mit derjenigen von $(101)_I$ und $(10\bar{1})_I$. Eine so hohe Beständigkeit der *Valonia*-Cellulose gegen Mercerisierung ist wahrscheinlich durch ihre grösseren Kristallinite und nicht einen höheren Kristallinitätsgrad bedingt.

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