

The Mercerisation of Cellulose

I. A Thermodynamic Discussion

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The cellulose occurring in nature contains a crystalline lattice of *Cellulose I* (native cellulose)*. After an intermediate swelling, for instance, with strong lye or sulphuric acid, and removal of the swelling agent at room temperature, the native cellulose is transformed into mercerised cellulose, earlier called "hydrate cellulose", a new modification with changed properties and containing a new crystalline lattice, *Cellulose II*. The process is called mercerisation or mercerising after John Mercer, who discovered and patented the process (1851). The industrial importance of Mercer's discovery was much increased by applying tension to the fibres during the treatment, a process developed by Horace Lowe (1890). In this process, shrinkage was prevented and the cotton acquired a silk-like luster and greater strength.

Mercerising has been the object of innumerable investigations, chiefly of technical or commercial aspects, and several monographs on mercerising have been published. The most comprehensive is that of Marsh¹, dealing mainly with the treatment of cotton with caustic soda. Mercerising with other agents (concentrated acids or salts, organic bases), and of other fibres is described in other more general handbooks or reviews on cellulose, especially those of Valko², Marsh and Wood³, Ott⁴, and Heuser⁵, which give a general description and references to the literature. Only facts of special importance for this paper will be outlined here with references to the original papers. Attention is focused on the mercerising of cotton and ramie with caustic soda, because comprehensive and reliable data on this reaction have been published. The aim is to give an interpretation of the mercerisation process, mainly from a thermodynamic point of view.

* There is in fact only one exception known, the sea algae *Halicystis*, reported by Sisson (*Science* 87 (1938) 350, *Contr. Boyce Thompson Inst.* 12 (1941) 31) to have cell membranes containing mercerised cellulose. These peculiar observations require further study.

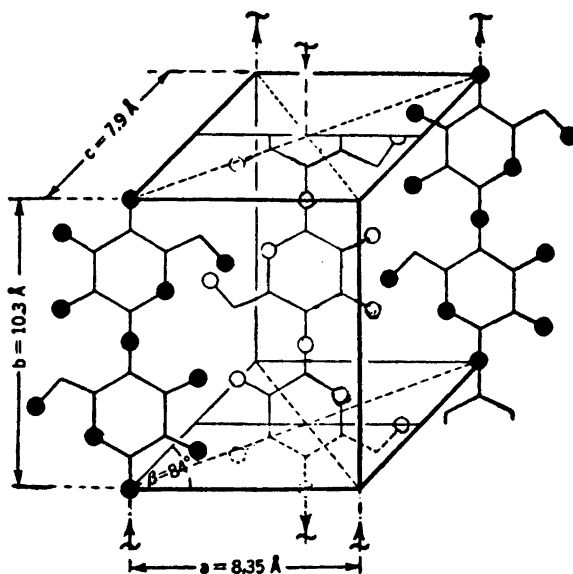


Fig. 1. The unit cell of native cellulose (*Cellulose I*) after Meyer, Mark, and Misch^{8,15}. Two edge chains are omitted for clarity.

I. CRYSTAL STRUCTURE CHANGES ON MERCERISING

The lattice transition on mercerising has been studied by many authors and surveyed in an excellent way by Mark⁶, in 1932. The structure conception described there has been further treated and frequently discussed (*cf.* Hermans⁷ for a review and for references).

A diagrammatic representation — after Meyer, Mark and Misch⁸ — of the monoclinic unit cell of native cellulose containing four glucose units is shown in Fig. 1. The transition of *Cellulose I* to *Cellulose II* (also monoclinic) caused by mercerising — implying $\sim 30^\circ$ rotation of the planes of the cellulose chains, related to the diagonal planes 101 and $10\bar{1}$ — is demonstrated in a projection perpendicular to the b -axis (Fig. 2) according to Andress⁹. The main features of these structure models may still be accepted¹⁰⁻¹² but the need for a detailed crystallographic investigation of the two lattices represents a serious lack. However, this work has now been started^{13,14}.

Published data of the unit cell dimensions have been collected in Table 1.

As pointed out by Hermans¹⁷ the cellulose chains in the lattice form long, flat cylinders (Fig. 3) with the hydrophilic OH-groups in limited regions at the edges. The lattice forces of *Cellulose I* and *II* are then of different origin in

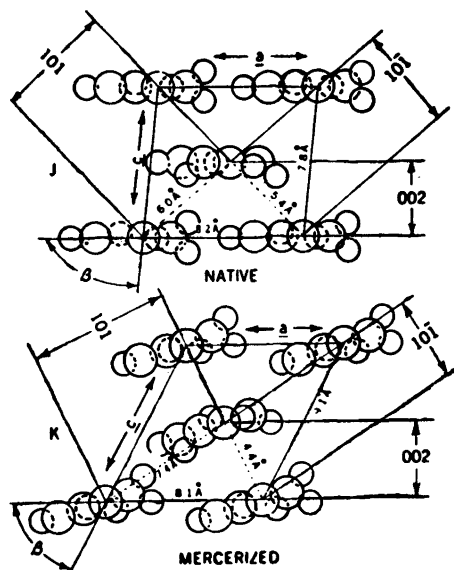


Fig. 2. Projections after Andress⁹ of the lower half of the unit cells of native and mercerized cellulose (Celluloses I and II) on the lower *ac*-plane of the cell.

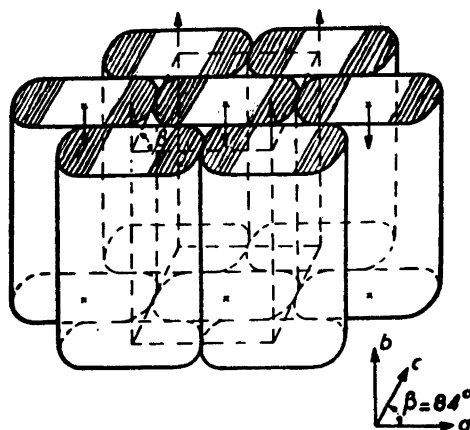


Fig. 3. Diagram of latticed molecules of native cellulose after Hermans¹⁷. The unit cell is indicated by broken lines. The regions containing the hydroxyl groups are shaded.

the directions of the three axes, as discussed in detail by Mark¹⁸. Most of the hydroxyl groups take part in formation of hydrogen bonds, as indicated by infrared absorption spectra¹⁹. The lattice forces hold the structure together so firmly, that it has recently been found possible to isolate crystalline cellulose particles, micelles, as well-defined rod-like morphological units²⁰. The hydroxyl groups of free cellulose chains have a considerable affinity for water, reacting exothermically with it. Inside the micelles, however, the hydroxyl groups are mainly saturated by inter- and intra-chain bond formation, making

Table 1. Lattice parameters of Cellulose I and II.

Lattice	Unit cell dimensions				Ref.
	<i>a</i>	Axes in Å		Angle β	
		<i>b</i>	<i>c</i>		
Cellulose I	8.30	10.30	7.96	84°	Meyer and Mark ^{8, 15}
»	8.23	10.28	7.84	84°	Andress ¹⁶
Cellulose II	8.14	10.30	9.14	62°	Andress ⁹

penetration of water molecules into the lattice impossible (*Cellulose I*) or possible to only a limited extent (*Cellulose II*)^{ci. 21}, and giving the cellulose micelles in aqueous colloidal solution a *hydrophobic* character²². This means, that the cellulose particles forming colloidal sols, although wetted by water, are coagulated by the addition of small amounts of electrolytes. In fact, penetration of water molecules into the lattice is not assumed for *Cellulose I*.^{*} But when alkali-cellulose (Na-cell.) is washed with cold water, two cellulose hydrates (water celluloses) are found, containing a lattice of *Cellulose II* into which water molecules have penetrated between the cellulose chains²³.

Unfortunately it is not possible to follow the mercerisation of cellulose as a pure lattice transformation of *Cellulose I* → *II*. All measurements to be used for this interpretation were made for fibres, assumed to contain both crystalline and non-crystalline cellulose.

II. ABSOLUTE CRYSTALLINITY

Mercerising of native cellulose causes a decrease in absolute crystallinity or lateral order according to measurements by physical, as well as chemical, methods. Representative figures from physical methods are those of Hermans *et al.* obtained by their own X-ray method²⁴. They measured a decrease in crystallinity from 70 to 47 per cent for ramie cellulose²⁴, and about the same values for wood pulp²⁵.

Representative crystallinity determinations, using chemical methods, are those of Nickerson²⁶ with boiling HCl—FeCl₃-solution, with the original values, corrected for a calculated recrystallization by Howsmon²⁷. This method gives a crystalline portion of 96 per cent (corrected 86 per cent) for cotton and 89 per cent (corrected 70 per cent) for mercerised cotton cellulose.

Chemical methods (hydrolysis, oxidation, formation of derivatives) generally give a lower percentage amount of noncrystalline cellulose than physical methods (X-ray diffraction, water sorption, deuterium exchange).

III. MICELLE DIMENSIONS

Closely associated with the decrease in crystallinity are changes in the micelle dimensions on mercerising. The micelles have been isolated by hydrolyzing with boiling 2.5 *N* sulphuric acid and washing the hydrocellulose with

* *Note added in proof:* In a recent paper, however, Legrand (*Compt. rend.* 226 (1948) 1983) concludes, from the relative intensity of the 002 and 101 X-ray reflections, that water molecules do penetrate the native cellulose lattice without affecting the unit cell dimensions.

distilled water. Measurements on electron micrographs showed that the micelle widths were unchanged after mercerisation ($\sim 70 \text{ \AA}$) and identical with the width of the micelle strings in the native and mercerised cellulose before hydrolysis. The weight averages of the micelle lengths decreased on mercerising from about 500 \AA to $350\text{--}400 \text{ \AA}$ for cotton cellulose, and to $250\text{--}300 \text{ \AA}$ for chemical grade wood cellulose²⁸. The measurements were made for micelles isolated through peptisation after hydrolysis. Due to degradation and a possible recrystallisation, these micelles cannot be considered as identical with the micelles of the solid state, *cf.* 27.

IV. DENSITY CHANGES

Density measurements of cellulose in water are misleading because of the interaction of cellulose and water, which results in a contraction of the system and a too high apparent density of cellulose or water. Density measurements in helium and in organic liquids, considered to be the most reliable, are collected in Table 2.

From the figures of Table 2 it is obvious that mercerising causes only a small density change, a net decrease in density (increase in volume) of about 1 per cent.

Table 2. Density (ρ) of cotton and ramie cellulose.

Sample	Medium	ρ	Medium	ρ	Ref.
Cotton, native	Helium	1.567	Toluene	1.550	Davidson ²⁹
» merc.	»	1.550	»	1.536	Davidson ²⁹
Ramie, native	Carbontetra- chloride	1.553			Hermans ³⁰
» merc.	»	1.543	(merc. under tension)		Hermans ³⁰
» »	»	1.526	» without »		Hermans ³⁰

From the unit cell dimensions of Table 1 the corresponding densities of the crystalline cellulose have been calculated to 1.60 (average) for native and 1.58 for mercerised cellulose. These calculated density values are ~ 2 per cent higher than those measured in helium. The comparison shows that the decrease in density on mercerising can at least partly be related to the lattice transition.

V. CHEMICAL CHANGES

So far as it is known, mercerising does not cause any change in the chemical composition of the cellulose *per se*. The glucose residues and the chains remain

unchanged with a possible slight depolymerisation. Impurities, oxycellulose, so-called hemicelluloses, and low molecular weight cellulose are partly extracted from the highly swollen alkali cellulose upon mercerising.

VI. HEAT EFFECTS

When cellulose is soaked in caustic soda, heat is evolved, an early observation in technical mercerising. Quantitative measurements of the amounts of heat have been made by Barratt and Lewis³¹, D'Ans and Jäger³², Neale³³, Tschilikin³⁴, Okamura³⁵, and Morrison, Boyd Campbell and Maass³⁶. The last two investigations are complementary and they will be discussed together here. The measurements were made for dried cellulose with adiabatic calorimeters.

The following thermodynamic symbols, according to Guggenheim³⁷, will be used:

U Energy content

H Heat content, enthalpy

G Gibbs free energy

P , V , S , and T are the general accepted symbols.

ΔH is negative for a process, where heat is evolved (exothermic). ΔG is negative for all natural (spontaneous) reactions.

The heat effect (ΔH) in the reaction between cellulose and caustic soda can be separated into three parts according to its origin:

- (a) heat of wetting the dry cellulose,
- (b) heat of reaction of the alkali with the wet cellulose, and
- (c) heat of a possible lattice transition.

$$\text{We have } \Delta H_T = \Delta H_a + \Delta H_b + \Delta H_c \quad (1)$$

Neale³³ has separated the ΔH_T into parts in another way, to suit his discussion.

Okamura³⁵ used purified ramie, dried to constant weight over P_2O_5 , one sample native and one sample mercerised (21.6 g NaOH pro 100 ml). For the reaction of 0.5 g dry cellulose with water or caustic soda of different concentrations, ΔH_T cal/g cellulose is represented in the diagram of Fig. 4 (curve 1 for native and curve 2 for mercerised cellulose). If the heat of wetting (ΔH_a) is subtracted (−3.66 and −6.09 cal/g for native and mercerised cellulose, resp.) the remainder represents $\Delta H_b + \Delta H_c$ (curve 3 and 4). For a concentration >20 g NaOH/100 cc the difference between the ΔH -values of curve 3 and 4

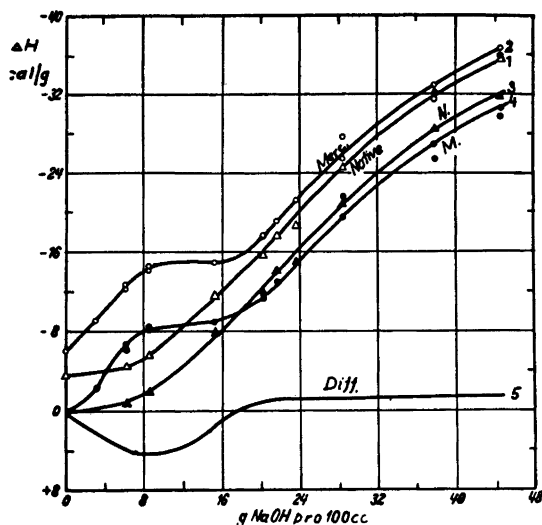


Fig. 4. The enthalpy effects (ΔH) of the reaction of native¹ and mercerized² ramie with caustic soda of different concentrations after Okamura³⁵.

seems to be constant (curve 5) and equal to the heat of transition ($\Delta H_c = -1.4$ cal/g) of wet native to wet mercerized cellulose, *i.e.*, the transition should be an exothermic reaction. This conclusion is not definite, however, as the standard error of the ΔH_c -values is of the order of magnitude of 0.4–0.8 cal/g (*cf.* the measurements indicated in Fig. 4). The ΔH -differences for concentrations < 20 g NaOH/100 cc indicate, that mercerized cellulose reacts more easily than native with diluted caustic soda, in conformity with other known facts.

The measurements of Morrison, Boyd Campbell, and Maass³⁶ are more accurate than those of Okamura³⁵. They were made for samples of cotton cellulose (standard cotton) in the native state and after immersion in sodium hydroxide solutions of concentrations from 5 to 18 %, washing and air-drying. All samples were finally oven-dried at 100° C. The heat of wetting with water was measured for all samples.

The heats of reaction for the pretreated samples were measured with a sodium hydroxide solution of a concentration the same as that employed in the pretreatment in each case. The results are summarized in Table 3.

The ΔH_T -values of col. 2 diminished by ΔH_a for the original cellulose (10.18 cal/g) and the ΔH_T -values of col. 3 by the corresponding ΔH_a -values of col. 4 give $\Delta H_b + \Delta H_c$ for original and pretreated cellulose, resp. The differences between these two series of ΔH -values represent the heat of trans-

Table 3. Heats of reaction (ΔH) of water and of sodium solutions with standard cellulose (cotton) and pretreated s.c.³⁶. The notations are according to equ. (1).

NaOH conc. in weight-%	Heat of reaction with standard cellulose, cal/g cotton	(ΔH_T) of NaOH sol. with s.c. pretreated with col. 1, cal/g cotton	Heat of wetting (ΔH_w) of pretreated s.c. by water, cal/g cotton
0	—	—	— 10.18
5.04	— 12.96	— 13.19	— 10.34
8.00	— 14.41	— 15.02	— 10.49
11.00	— 17.30	— 18.63	— 11.87
13.18	— 22.57	— 27.69	— 15.48
15.69	— 28.80	— 35.22	— 18.15
18.14	— 30.56	— 37.19	— 18.79

formation (ΔH_c) of wet native to wet mercerised cellulose, analogous to the interpretation of Okamura's measurements³⁵. In the diagram of Fig. 5 the ΔH_c -values are plotted as a function of the NaOH-concentration (curve 1). This quantity is close to zero until at 12 % NaOH; after mercerisation it is about -2 cal/g (Fig. 5), with a standard error of 0.1—0.3 cal/g. Morrison, Boyd Campbell, and Maass³⁶ have defined the quantity $-(\Delta H_{T \text{ merc.}} - \Delta H_{T \text{ native}})$ as "heat of mercerisation", plotted in curve 2 of Fig. 5. This quantity is denoted ΔH_{dry} , as it apparently corresponds to the heat of reaction in the hypothetical transition of dry native to dry mercerised cellulose. Such an interpretation is inconvenient and misleading. It is preferable to treat the wet native cellulose as the initial state and define the ΔH_c referring to wet cellulose as the heat of mercerisation for the following reasons:

1. cellulose is deposited in nature as wet native cellulose,
2. wet cellulose is better defined than dry cellulose as the last traces of wetting agents are very difficult to remove and it is difficult to keep the cellulose free from the wetting agent during treatment, and
3. mercerisation is reported only for systems, where the cellulose is wetted, with water or an organic solvent.

The changes in enthalpy (ΔH) in soaking native (A) and mercerised (B) cellulose in 18.14 % NaOH³⁶ are represented in the diagram of Fig. 6. Wet native cellulose has been assigned a $\Delta H = 0$. The lowest enthalpy level ($\Delta H = -20.38$ cal/g) is reached for cellulose soaked in lye, apparently identical, if native or mercerised cellulose are the starting materials. Dry cellulose has the highest enthalpy ($+10.18$ and $+16.81$ cal/g for native and mercerised,

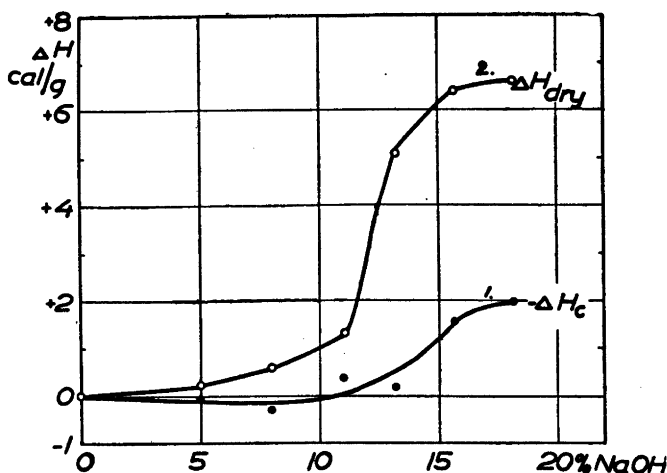


Fig. 5. The heat of transformation of native to mercerised cellulose, curve 1 for wet samples and curve 2 for dry samples plotted after measurements of Morrison, Boyd Campbell and Maass³⁶

resp.). The wet celluloses are on an intermediate level with $\Delta H_{\text{Cell. II wet}} = -1.98$ cal/g in fairly good agreement with Okamura's measurements. This enthalpy effect (ΔH_c) is small compared to the total effects (ΔH_T) for the cellulose-lye-reaction. We define ΔH_c as composed of two contributions, one ΔH_{c1} from the lattice transition *per se* (an interchain reaction) and one ΔH_{c2} from the reaction of the phases with water, but for our purpose it is not even necessary to know the sign of these two contributions. We have

$$\Delta H_c = \Delta H_{c1} + \Delta H_{c2} \quad (2)$$

From the measurements discussed it is concluded that the transformation of wet native to wet mercerised cellulose is an exothermic process with a small enthalpy change ($\Delta H \sim -2$ cal/g cellulose).

VII. ENTROPY EFFECTS

No absolute entropy values of cellulose have been measured or calculated so far. The entropy effects in the reaction of cellulose with water and other vapors have been studied, reviews have been made by Valko³⁸, and Rees³⁹, and papers have been published recently by Wahba⁴⁰, and Guthrie⁴¹. Nothing seems to be written on the entropy effects of mercerisation.

If a more accurate picture of the morphology and structure of native and mercerised cellulose, than at present, were available, it would be possible to calculate the entropy of mercerisation theoretically using statistical thermodynamics. Such calculations could be performed by analogy with those for high polymers (*cf.* Bawn⁴² for a review). In our case, however, it is sufficient to find out, if the entropy of cellulose increases or decreases on mercerising.

As reviewed in sections 3, 4, and 5, mercerising definitely causes a lower absolute crystallinity, *i.e.* a decrease in the lateral order of the chains, as indicated from measurements with physical and chemical methods. The density is lowered and the crystalline regions (the micelles) are partly divided into fragments. The orientation of the micelles parallel to the fibre axis decreases upon mercerisation without tension⁴³. All these measured effects indicate a transformation of the cellulose into a state of greater disorder and consequently of a higher probability, *i.e.*, an increase in the entropy function most probably occurs at room temperature ($\Delta S_{\text{merc.}} > 0$). This must be the case both for dry and wet cellulose, according to the crystallinity and accessibility measurements, made for these two states.*

VIII. THERMODYNAMIC INTERPRETATION

Mercerisation of cellulose with caustic soda is possible to perform as an adiabatic process, if the temperature does not exceed 50–60° C^{*cf.* 4, p. 274}. The ΔH -measurements are carried out under such conditions^{35, 36} within a small temperature interval. As the entropy function increases in the reaction (ΔS positive according to Sect. 7), it follows that the adiabatic mercerisation is a spontaneous (natural) process.

For an isothermal reaction the following relation holds according to the definitions of the symbols:

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

To calculate the ΔG for the isothermal transformation of wet native to wet mercerised cellulose fibres it is necessary to follow a reversible way from the initial (native) to the final (mercerised) state. Such a calculation is not possible from the data presented in Sects. 6 and 7, as the values of ΔH and ΔS

* The entropy discussion is strictly valid only if the mercerisation leaves the cellulose chemically unchanged. A slight depolymerisation of the chains (comp. sect. 6) is the only chemical effect known. As entropy is primarily a function of the order of the chain segments (glucose units) it cannot be affected very much by the breaking of a few bonds (the order of magnitude is one broken bond per 500–1 000 glucose units).

have been determined for the spontaneous, adiabatic process only. Additional information, for instance of the heat capacity for the wet phases, which is necessary for the calculation of ΔG according to equ. (3), is not yet available.

From this discussion it is concluded, that the transformation of wet native to wet mercerised cellulose is a natural process at room temperature and atmospheric pressure and that wet native cellulose is in a metastable state under these conditions.

Mercerisation causes a decrease in the total energy (ΔU) of the cellulose, too. Because of the small volume change upon mercerisation (Sect. 4), ΔU — at atmospheric pressure — is practically identical with the decrease in enthalpy (ΔH).

As already pointed out (Sect. 2) this thermodynamic discussion is valid only for the mercerisation of wet cellulose fibres assumed to contain both crystalline and non-crystalline substances. So far it is not possible to treat the transition of the pure lattices of *Cellulose I* \rightarrow *II*.

IX. STABILITY OF NATIVE AND MERCERISED CELLULOSES

The conclusion that wet native cellulose is in a metastable and wet mercerised in a stable state at room temperature is already verified by experiment. Hess, Kiessig, and Gundermann⁴⁴ observed that bone-dry cellulose fibres, treated in a ball-mill for several hours, lost their lattice order completely. When these fibres were treated with water at room temperature, they re-formed a lattice, which was invariably *Cellulose II*, even if the original cellulose was native. These findings are quite analogous to the well established fact that an intramicellar swollen cellulose (with caustic soda solutions, organic bases, cuprammonium, strong sulphuric acid or zinc chloride solutions) on deswelling at room temperature always recrystallises with the lattice of *Cellulose II*. Mercerised cellulose, however, doesn't seem to be stable at higher temperatures. It has been shown⁴⁵, that high temperature treatment (250° C) of regenerated cellulose fibres (containing the lattice of *Cellulose II*) with glycerine, glycol, formamid or other liquids of strong polarity causes a transition to *Cellulose I*. The transition was more complete, if the fibres were pre-swollen as alkali-cellulose. Kubo's results are supported by Hermans' observations⁴⁶, that saponification of cellulose acetate in 2 *N* ammonia solution at 100° C is accompanied by a partial transformation into native cellulose. No transformation into mercerised cellulose at high temperature is described in the literature. Some confusion exists on the true nature of the cellulose lattice regenerated from *Cellulose II* at high temperature. Hess, Kiessig and Gundermann⁴⁴

hold the view that a new lattice, *Cellulose IV*, high temperature (HT) cellulose, and not *Cellulose I* is formed by heating in glycerine. The lattice of *Cellulose IV* is reported to resemble that of *Cellulose I* very closely, the *a* and *c* axes are vertical and the unit cell accordingly rhombic, but the X-ray diagrams published to support the two views show too low a resolving power for a definite conclusion. Further experiments should be made on this point, as the problem is also of thermodynamic interest. From his experiments, Kubo⁴⁵ assumes that the stability of *Celluloses I and II* at different temperatures follows approximately the diagram of Fig. 7 (the ordinate should be the Gibbs free energy (*G*), not the "stability" of Kubo). If native cellulose is really stable and mercerised cellulose really metastable at high temperature, the curves ought to intersect at an intermediate temperature, at which $\Delta G = 0$ and $\Delta H = T \Delta S$ for a lattice transition.

Conversion experiments of mercerised to native cellulose have also been performed by Meyer and Badenhuisen⁴⁶. They obtained a partial conversion through heating to 200–300°C with water, too. Their conclusion was that "at least over the range of temperatures covered by these experiments native cellulose is the stable form and hydrate cellulose the non-stable". The velocity of transformation, however, was assumed to be very low (not measureable) at low temperatures. These views have obviously no support from later measurements (Sect. 2–7) and their thermodynamic interpretation (Sect. 8, 9) and are then to be abandoned.

X. DISCUSSION

Work on the lattice transformation of cellulose is of direct importance as the change in fibre properties on mercerising, for example, the penetration and regain of water, accessibility to dyestuffs, and chemical reagents, are due to the phenomenon. It is of an indirect importance in many respects, too. Without a doubt, investigations of the lattice transition *per se* has increased the general knowledge of cellulose, its properties and reactions. Mercerisation is still the best evidence of an intra-micellar swelling of native cellulose. Its thermodynamic interpretation as an exothermic, natural process explains among other things the negative temperature coefficient of the alkali swelling of cellulose.

Furthermore, the thermodynamic conditions of lattice stability seem of great importance for a proper understanding of the formation of cellulose in nature. As already pointed out, cellulose is always formed with the lattice of *Cellulose I*, *i.e.*, in a metastable state. This is true for fibre cellulose in plants and for animal cellulose (tunicin) as well as bacterial cellulose, formed extracellularly as water-swollen gels. Only one exception is known (comp. a note to Sect. 1). Many authors have assumed that cellulose is synthesised as chains,

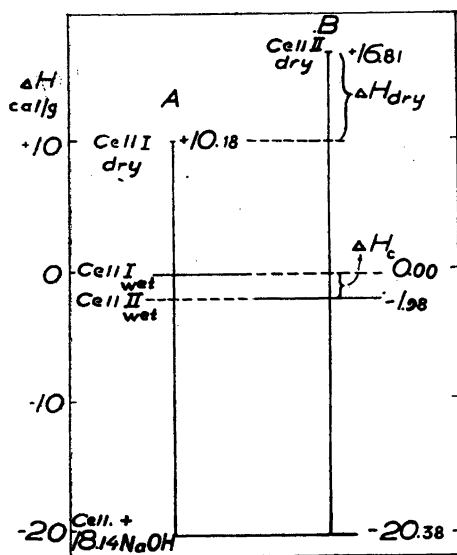


Fig. 6. The enthalpy effects (ΔH) on wetting and soaking native (A) and mercerised (B) cellulose in 18.14 NaOH; after measurements of Morrison, Boyd Campbell and Maass³⁶.

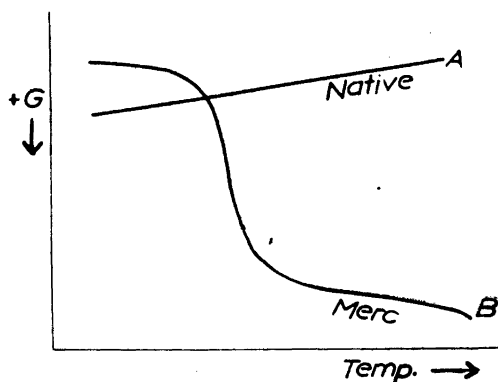


Fig. 7. Hypothetical diagram after Kubo⁴⁵ of the Gibbs free energy of native and mercerised cellulose at different temperatures.

which should aggregate and partly crystallize, forming a micellar framework⁴⁷. Such a conception is doubtful for the following reasons. A crystallization of free chains or a deswelling of intra-micellar swollen cellulose at room temperature in the presence of water *in vitro* invariably and rapidly leads to a cellulose containing the lattice Cellulose II. This is quite reasonable from a thermodynamic point of view (Sect. 10). On the contrary, an assumed crystallization of chains *in vivo* must proceed in quite another way as it apparently leads to a cellulose, containing the lattice Cellulose I, *i.e.*, to a metastable state, never observed to be formed *in vitro* in the presence of water at room temperature. This fact makes the assumption of a crystallization of free chains in the water-rich system of the living cell very improbable. It is much more reasonable, then, to assume that the lattice of the native micelles (Cellulose I) is formed from chains under influence of a specific enzyme system or by a direct synthesis in the cell^{28,49}. These assumptions on the formation of cellulose are also made probable by the fact that the micelles and the micelle strings have a uniform width ($70 \pm 15 \text{ \AA}$) according to measurements on electron micrographs^{Cf. 20, 28}.

SUMMARY

1. Based on published data, the enthalpy (ΔH) and entropy (ΔS) effects upon mercerisation of cellulose have been discussed and a thermodynamic interpretation of the mercerising has been proposed.

2. If the author's views (p. 110) are accepted and applied on available data, the conversion of wet native to wet mercerised cellulose is an exothermic (ΔH negative) and natural (ΔS positive) process.

3. The stability of native and mercerised cellulose at different temperatures, conversion experiments *in vitro* and the synthesis of cellulose *in vivo* have been discussed in connexion with the thermodynamic interpretation.

This investigation is part of a research programme on cellulose carried out at the Institute of Physical Chemistry, University of Uppsala, under supervision of Professor The Svedberg and in collaboration with the Swedish cellulose firms *Billeruds AB*, *Mo och Domsjö AB*, *Stora Kopparbergs Bergslags AB*, *Svenska Cellulosa AB* and *Uddeholms AB*.

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