

The composition of alkali cellulose: a new concept

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A concept of reacting structural fractions is presented to discuss NaOH- and H₂O-sorption of cellulose up to a lye concentration of 18% NaOH. The reacting structural fraction has been estimated by wide-angle X-ray scattering combined with a consistent application of a two-phase model (crystalline-non-crystalline) to the cellulose supermolecular structure.

As a result, crystalline Na-cellulose I is characterized by an invariable composition definitely below 1 mol NaOH per mole of anhydroglucose units (AGU), whereas non-crystalline regions show a variable composition giving a saturation value of 2 mol NaOH per mole AGU. The swelling maximum of cellulose is determined mainly by the course of water-sorption in the non-crystalline regions.

(Keywords: cellulose; NaOH-sorption; H₂O-sorption; reacting structural fraction)

INTRODUCTION

The technical importance of alkali cellulose as a turntable in cellulose derivatization and as an intermediate in the mercerization of cotton has stimulated research into the formation and structure of this cellulose compound for over a century. But, in spite of a host of experimental results obtained by instrumental (wide-angle X-ray scattering, solid state n.m.r.) as well as by chemical methods, there are still open questions of a fundamental nature about the mode of interaction between cellulose and aqueous NaOH as well as about the chemical composition and physical structure of alkali cellulose. In our opinion, controversial discussions about alkali cellulose composition are mainly caused by the fact that cellulose and alkali cellulose are each considered as a continuum with homogeneous structure, and that the existence of regions of different states of order is not appropriately considered.

In this paper, the supermolecular structure of cellulose is taken into account in discussing alkali and water sorption of cellulose. Starting from a two-phase model of cellulose physical structure with ordered and disordered regions, a concept of *reacting structural fraction (RSF)* is developed to subdivide the integral sorption values into parts that can be correlated to definite structural regions, thus providing a deeper understanding of the interaction between cellulose and aqueous alkali. This new concept is tested by using integral NaOH- and H₂O-sorption data¹ as well as results of wide-angle X-ray scattering measurements (WAXS)^{2,3} obtained after reacting a scoured and bleached linters cellulose ($DP \approx 1600$) with aqueous alkali in the concentration range from 0 to 18% by weight.

ESTIMATION OF REACTING STRUCTURAL FRACTIONS OF CELLULOSE FROM WAXS DATA

The concept of *RSF* originates from the experimental fact that—dependent on NaOH concentration in the steeping lye—a variable number of AGU is participating in the interaction between cellulose and aqueous alkali. So to discuss the alkali and water sorption, it seems unjustified to relate the amount of NaOH and H₂O sorbed to the total mass of cellulose. These amounts should be better correlated to the *RSF* only that really is participating in the interaction.

This approach seems reasonable insofar as a lattice transformation of crystalline cellulose I to Na-cellulose I (notation used in ref. 5) does not take place below a NaOH concentration of about 10% in the steeping lye, and in the lattice transition range of lye concentration between about 10 and 14% NaOH both crystalline cellulose I and crystalline Na-cellulose I coexist, as revealed by the WAXS pattern.

The estimation of *RSF* dependence on steeping lye concentration is based on a two-phase model⁴ with crystalline and non-crystalline regions that can be adequately quantified by WAXS measurements³. According to this model, an appropriate *RSF* is composed of: the anhydroglucose units located in the non-crystalline, disordered regions; crystalline regions of cellulose already transformed to the Na-cellulose I lattice at the lye concentration in question; the surfaces of the remaining cellulose I crystallites.

A definitely unreactive, inert structural fraction is formed by the interior of cellulose I crystallites still existing at the lye concentration in question. According to

this, the *RSF* at very low lye concentration is only represented by the non-crystalline regions of cellulose, and it reaches a value of 100% at lye concentration above 14%, caused by a complete lattice transition to Na-cellulose I. The non-crystalline (disordered) fraction of the sample can be obtained from X-ray crystallinity measurement. The fraction of cellulose I and Na-cellulose I at any lye concentration in question is provided by a quantitative phase analysis.

Chain segments arranged at the surface of cellulose I crystallites are neglected for *RSF*, in first approximation. Even with the assumption of full accessibility of lateral surfaces of crystallites, the high degree of binding in the surface and with interior molecules will reduce the reactivity compared to a freely accessible chain segment.

The degree of crystallinity and the relative amounts of crystalline cellulose I and crystalline Na-cellulose I were obtained by appropriate WAXS methods by using isotropically prepared samples and applying a horizontal diffractometer in a symmetrical transmission technique with $\text{CuK}\alpha$ radiation. The samples had been fixed between two 15 μm polyester foils during the diffraction experiments. Diffracted intensity was registered stepwise and corrected by considering, among other things, the scattered radiation of the polyester foils. Details of the WAXS technique employed for estimating the degree of crystallinity and the relative amounts of cellulose I and Na-cellulose I have already been published^{2,3} and shall be reviewed only briefly here as an essential step in understanding the discussion that follows.

For calculating the degree of crystallinity

$$x_c = m_c/m_t \quad (1)$$

where m_c is the mass of the crystalline part of the sample and m_t is the total mass, samples of cellulose regenerated from alkali cellulose by neutralization, washing and air-drying have been used. The WAXS data obtained in an angular range $4^\circ \leq 2\theta \leq 104^\circ$ were evaluated by the method of Ruland⁶ and Vonk⁷. Depending on the steeping lye concentration, x_c varies only slightly, with a tendency to decrease with increasing NaOH concentration (*Figure 1*). The non-crystalline part ($1 - x_c$) of the sample is totally counted in *RSF*. The estimation of the relative amounts of crystalline cellulose I and Na-cellulose I in the alkalinized samples was achieved by a quantitative analysis² of the different scattering phases. This kind of phase analysis is based on a weighted superposition of the two WAXS curves of the original and of the final state of the sample after complete conversion to alkali cellulose. In our experiments with cotton linters, a sample treated with 10% aqueous NaOH, which contained only cellulose I as crystalline phase, was applied to represent the original state (scattering phase A). The final state of complete transformation to alkali cellulose was realized by treating the cellulose sample with 18% aqueous NaOH (scattering phase B). With the relative mass x^A of scattering phase A and x^B of scattering phase B the relation $x^A + x^B = 1$ holds true. The term x^B in terms of lye concentration is shown in *Figure 1*, where x^B , by definition, comprises both the crystalline and the disordered part of alkali cellulose. The curve in *Figure 1* shows the large slope of x^B in the range of lye concentration between 10.5 and 13% NaOH. With x_c^B as the degree of crystallinity of scattering phase B, the crystalline part of alkali-cellulose is given approximately by $x^B \times x_c^B$.

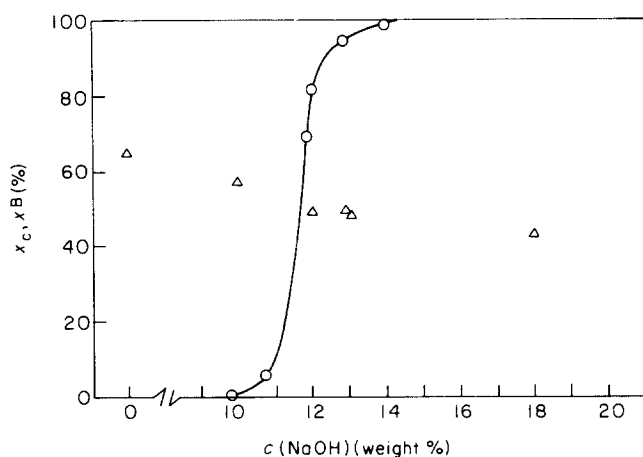


Figure 1 Degree of crystallinity, x_c (Δ), and fraction x^B of scattering phase B (\circ) versus NaOH concentration

The reacting structural fraction at a given concentration of steeping lye is then obtained additively according to

$$RSF = (1 - x_c) + x^B \times x_c^B \quad (2)$$

With the premises discussed above, the *RSF* dependence on lye concentration $c(\text{NaOH})$ can alternatively be obtained from the non-reacting fraction of the cellulose structure, employing the same set of experiments:

$$\begin{aligned} 1 - RSF &= x_c && \text{for } c(\text{NaOH}) < 10\% \\ 1 - RSF &= x^A \times x_c^A && \text{for } c(\text{NaOH}) \geq 10\% \end{aligned} \quad (3)$$

The expression $(1 - RSF)$ denotes the fraction of crystalline cellulose I in the sample, with x_c^A as the degree of crystallinity of scattering phase A. Within the limits of experimental error, calculations of *RSF* by equation (2) and by equation (3) are equivalent for the following discussion. Referring to *Figure 2*, which demonstrates the increase of *RSF* with $c(\text{NaOH})$, the slight increase at $c(\text{NaOH}) < 10\%$ is obviously caused by an increasing fraction of disordered chain segments. The steep increase of *RSF* at $c(\text{NaOH}) > 10\%$ reflects the lattice transformation from cellulose I to Na-cellulose I. At $c(\text{NaOH}) > 14\%$ all of the chain segments have participated in the reaction. To facilitate the subsequent discussion, the range of *RSF* in *Figure 2* may be subdivided into area I and area II, where I symbolizes the area of originally non-crystalline chain segments with a constant value $RSF_n = \text{const.}$, independent of $c(\text{NaOH})$, while II denotes that part, $RSF_c(c(\text{NaOH}))$, of the ordered regions in the original sample reacting with NaOH and increasing with $c(\text{NaOH})$. Area III symbolizes the non-reacting, inert fraction $I(c(\text{NaOH}))$ of the sample at the concentration in question. The condition of normalization is given by

$$RSF_n + RSF_c(c(\text{NaOH})) + I(c(\text{NaOH})) = 1 \quad (4)$$

DETERMINATION OF NaOH- AND H₂O-SORPTION

Our method of differential titration of the liquid (steeping lye) phase before and after sorption with addition of an

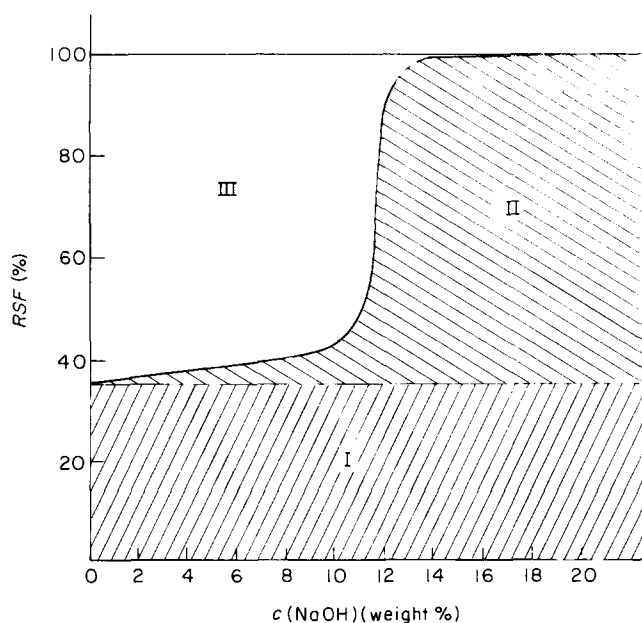


Figure 2 Reactive structural fractions versus concentration

inert electrolyte (NaCl) to the lye has already been discussed in detail in ref. 1. The method combines the advantages of the solid phase analysis given by Schwarzkopf⁸ and of the classical differential titration of the liquid phases according to Vieweg⁹. Results obtained with cotton linters by differential titration of NaOH and NaCl in the lye before and after sorption and a subsequent evaluation based on mass balances are given in Figure 3, the curves denoting NaOH- and H₂O-sorption per AGU related to the whole sample (integral sorption $S(\text{NaOH})$, $S(\text{H}_2\text{O})$) in terms of $c(\text{NaOH})$ in the equilibrium state after sorption. The agreement with the Schwarzkopf curve, included in Figure 3 for comparison, is very satisfactory, but our method is definitely less time-consuming and obviously more precise and reliable due to our avoidance of additional premises necessary for the Schwarzkopf method¹.

APPLICATION OF THE RSF CONCEPT TO ALKALI AND WATER SORPTION OF LINTERS CELLULOSE

In our opinion, a comprehensive interpretation of sorption processes onto cellulose implies correlating integral sorption data (Figure 3) obtained experimentally to the appropriate reacting structural fractions. This correlation will now be discussed with regard to alkali and water binding onto linters cellulose at 20°C in a concentration range of steeping lye between 0 and 18% NaOH, by employing RSF and sorption data discussed in the previous two sections.

Alkali sorption

NaOH-sorption related to the appropriate RSF (specific NaOH-sorption $S(\text{NaOH})/\text{RSF}$) in terms of lye concentration is shown in Figure 4 in comparison with the integral sorption values $S(\text{NaOH})$. As is expected from the considerations given in the last section, at a low concentration of NaOH in the lye, the specific NaOH-sorption $S(\text{NaOH})/\text{RSF}$ significantly exceeds the integral sorption value, $S(\text{NaOH})$, as the alkali sorbed at low concentration is fixed mainly in the non-crystalline

regions of the cellulose moiety. At a lye concentration corresponding to the beginning of lattice transition, a maximum of $S(\text{NaOH})/\text{RSF}$ near 1 mol NaOH per mole AGU is found, followed by a minimum as lattice transition progresses. The decrease of $S(\text{NaOH})/\text{RSF}$ between 11 and 13% NaOH in the lye is due to the fact that the reacting structural fraction increases more steeply in this range of lattice transition than the integral sorption $S(\text{NaOH})$. Above 13% NaOH in the lye, the RSF reaches at 100%, and the specific alkali sorption becomes identical with the integral sorption.

Most relevant to a further discussion is the definite decrease of specific alkali sorption from 0.9 down to about 0.6 mol NaOH per mole AGU in the range of lattice transition. This low, average specific alkali sorption at a lye concentration of about 12% obviously rules out a ratio of one or even more than one mole of NaOH per AGU in the crystalline alkali cellulose, as assumed in several previous publications¹⁰⁻¹². The sharp decrease of $S(\text{NaOH})/\text{RSF}$ in this range suggests, on the contrary, the formation of an alkali cellulose with a molar ratio of NaOH per AGU definitely below 1. The ratio of 1 often cited in the literature^{5,11,12} for Na-cellulose I corresponds to a composition compatible with a completely filled volume of the lattice cell if an amount of 3 mol of water per mole AGU is included⁵. This ratio of one mole NaOH per

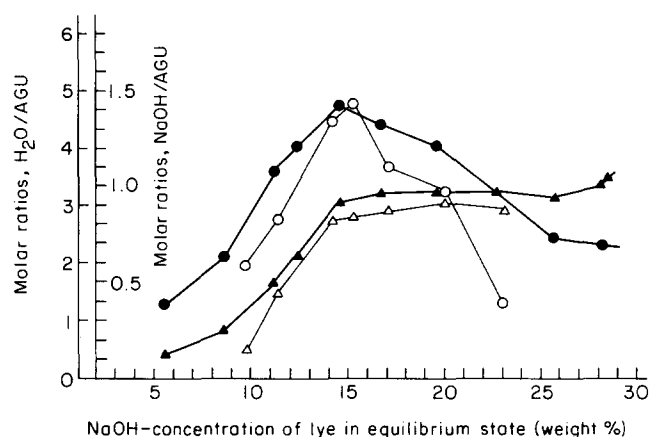


Figure 3 Integral NaOH- and water-sorption of cellulose from aqueous NaOH-solution by the methods^{1,8}: \blacktriangle , NaOH-sorption¹; \triangle , NaOH-sorption⁸; \bullet , H₂O-sorption¹; \circ , H₂O-sorption⁸

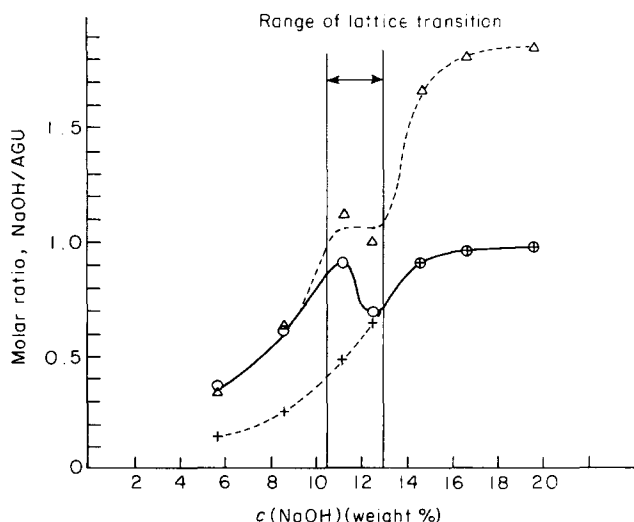


Figure 4 Average specific NaOH-sorption (\circ) of cellulose in comparison with integral sorption (+) and specific sorption of non-crystalline fraction (\triangle)

mole AGU corresponds to the integral sorption value at a lye concentration between 16 and 20%. But with the assumption of a higher water content, also a lower NaOH/AGU molar ratio may correspond to a completely filled volume of the lattice cell. Thus it seems to be reasonable for an interpretation of the course of $S(\text{NaOH})/RSF$ with $c(\text{NaOH})$ to assume a NaOH/AGU ratio of maximum 0.5, with an appropriate higher water content in the unit cell of Na-cellulose I. Assuming a molar NaOH/AGU ratio of $S^c(\text{NaOH})=0.5$ for the crystalline part, RSF_c , this ratio for the non-crystalline part, RSF_n , is then given by the equation

$$S^n(\text{NaOH}) = \frac{1}{RSF_n} (S(\text{NaOH}) - S^c(\text{NaOH}) \times RSF_c) \quad (5)$$

The dependence of $S^n(\text{NaOH})$ on $c(\text{NaOH})$ is demonstrated in Figure 4 as a separate curve (open triangles). With $S^c(\text{NaOH})=0.5$ for the composition of crystalline Na-cellulose I, an approximately constant value of $S^n(\text{NaOH})$ is obtained in the range of lattice transition. (A decreasing NaOH-sorption with increasing concentration of lye seems rather meaningless.) With a further increase of $c(\text{NaOH})$ and the assumption of the constant value $S^c(\text{NaOH})$ a rather steep increase of $S^n(\text{NaOH})$ is found. The plateau of the integral alkali sorption at a level of about 1 mol NaOH per mole AGU in the concentration range $15\% < c(\text{NaOH}) < 20\%$ is obviously caused by some kind of saturation of the disordered regions with NaOH at a level of about 2 mol NaOH per mole AGU.

To summarize the consequences of our concept, the dependence of specific sorption of NaOH onto cellulose on steeping lye equilibrium concentration $c(\text{NaOH})$ can be tentatively interpreted by assuming two fractions of cellulose structure differing in binding capacity for NaOH, i.e. a crystalline part with a constant composition of maximum 0.5 mol NaOH per mole AGU and a disordered part with a variable composition depending on $c(\text{NaOH})$, levelling off at about 1.9 mol NaOH per mole AGU at high $c(\text{NaOH})$.

Water sorption

The specific sorption of water $S(\text{H}_2\text{O})/RSF$ is compared with the integral sorption values $S(\text{H}_2\text{O})$ versus $c(\text{NaOH})$ in Figure 5. The course of specific water sorption with $c(\text{NaOH})$ obviously is analogous to that of specific alkali sorption. At low $c(\text{NaOH})$, the specific water sorption $S(\text{H}_2\text{O})/RSF$ exceeds the integral values, arriving at a maximum at the beginning of lattice transition, decreasing within the transition range merging in the integral sorption curve at 13–14% NaOH in the lye and finally rising to a second maximum at 14–15% NaOH, well known from the integral water sorption curve^{1,8}. As a premise for further discussion we again assume a constant composition independent of $c(\text{NaOH})$ for the crystalline Na-cellulose I, not only with regard to the molar ratio NaOH/AGU, but also with regard to that of $\text{H}_2\text{O}/\text{AGU}$. Taking into account the results of NaOH-sorption and their interpretation given above, a value of $S^c(\text{H}_2\text{O})=3.5$ seems to be very probable for crystalline alkali cellulose I, as a composition of 0.5 mol NaOH: 3.5 mol H_2O :1 mol AGU corresponds well to a completely filled volume of the Na-cellulose I unit cell⁵.

On the basis of this composition for crystalline Na-cellulose I, the water content $S^n(\text{H}_2\text{O})$ of disordered alkali cellulose as a function of $c(\text{NaOH})$ is given by

$$S^n(\text{H}_2\text{O}) = \frac{1}{RSF_n} (S(\text{H}_2\text{O}) - S^c(\text{H}_2\text{O}) \times RSF_c) \quad (6)$$

This course of $S^n(\text{H}_2\text{O})$ with $c(\text{NaOH})$ is also shown in Figure 5 as a separate curve. As can be seen from that curve, the main maximum of $S^n(\text{H}_2\text{O})$ also coincides with the beginning of lattice transition just as the maximum of average specific water sorption $S(\text{H}_2\text{O})/RSF$, but reaches, at ca. 8 mol H_2O per mole AGU a distinctly higher level. With further increases in the concentration of lye, $S^n(\text{H}_2\text{O})$ decreases and then reaches a second, somewhat lower maximum of about 7 mol H_2O per mole AGU, which nevertheless exceeds the maximum value of integral water sorption considerably.

The well known swelling maximum of cellulose, i.e. the maximum volume increase at the beginning of lattice transition, may reasonably be correlated to the principal maximum of $S^n(\text{H}_2\text{O})$ at about the same $c(\text{NaOH})$, if we assume that water binding in the disordered regions leads to a larger specific increase of volume than water sorption in the highly ordered crystalline regions.

The curve of $S^n(\text{H}_2\text{O})$ with $c(\text{NaOH})$ can be still better understood by plotting the ratio of $S^n(\text{H}_2\text{O})/S^n(\text{NaOH})$ versus $c(\text{NaOH})$ (cf. Figure 6). For comparison, an inverse lye-concentration as a molar ratio $\text{H}_2\text{O}/\text{NaOH}$ is plotted against $c(\text{NaOH})$. $S^n(\text{H}_2\text{O})/S^n(\text{NaOH})$ shows a monotonous curve, as to be expected for a cellulose structure with chain segments freely accessible to the aqueous alkali.

CONCLUSIONS

The RSF-concept leads to a more detailed understanding of NaOH and water sorption onto cellulose. According to this concept and assuming an invariant composition of crystalline Na-cellulose I, a molar ratio of (maximum) 0.5 NaOH:(minimum) 3.5 H_2O :1 AGU holds true. Disordered cellulose always sorbs more NaOH and water than crystalline cellulose, the composition of disordered alkali cellulose being dependent on $c(\text{NaOH})$.

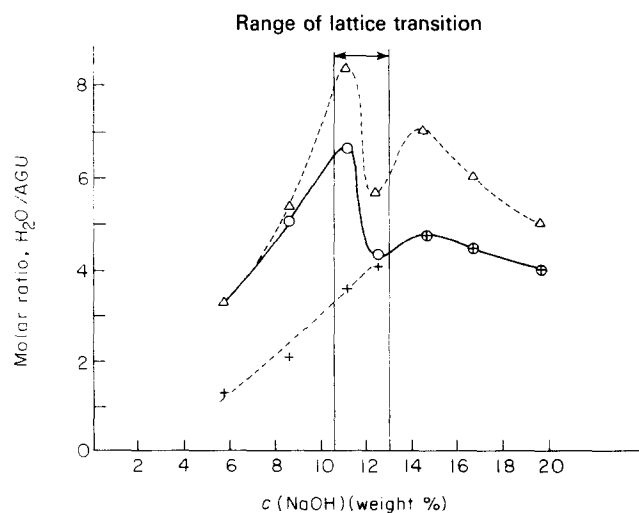


Figure 5 Average specific H_2O -sorption (O) of cellulose in comparison with integral sorption (+) and specific H_2O -sorption of non-crystalline fraction (Δ)

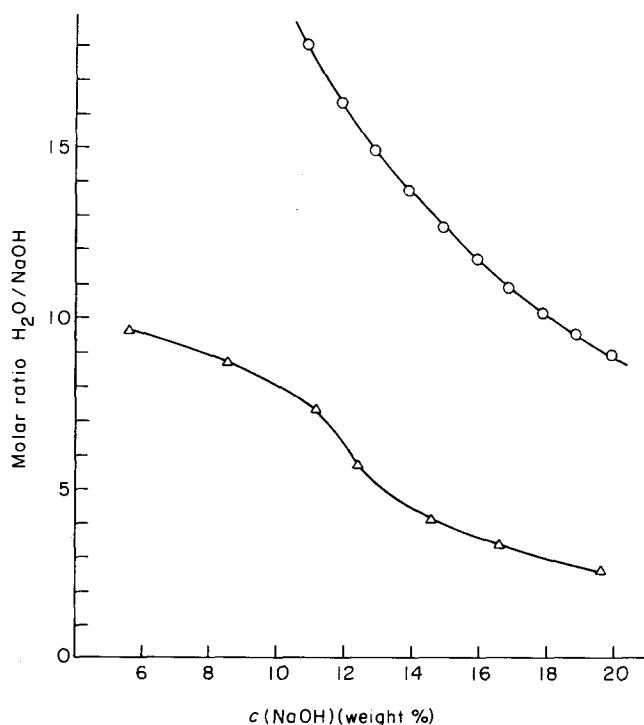


Figure 6 Molar ratios of H₂O/NaOH in cellulose non-crystalline structural fraction (Δ) and in the equilibrium lye (O)

In the concentration range $17\% < c(\text{NaOH}) < 20\%$, relevant in the viscose process, alkali sorption of the disordered regions reaches a level of saturation at about 2 mol NaOH per mole AGU. The course of water sorption in disordered alkali cellulose with $c(\text{NaOH})$ exhibits two maxima, the first, principal one coinciding with the swelling maximum of cellulose at the beginning of lattice transition, and occurring at a definitely lower lye concentration than the maximum of the integral water sorption curve.

The results presented here are in some contradiction to the generally assumed alkali cellulose composition of 1 NaOH:3 H₂O:1 AGU derived from integral sorption data. However, our results are in agreement with the experimental facts that:

(i) The integral NaOH and water sorption curves depend on state of order and lateral dimensions of the crystallites in the sample^{3,4,13}.

(ii) Recent experimental results by Käufer¹⁴ permit the conclusion of two different rates of reaction in the alkalization process, which might be associated with the reaction of aqueous alkali with different structural

fractions of the cellulose sample. The *RSF* concept might be employed in kinetic studies also with a good chance of success.

So far our new concept has been applied to steeping lye concentration up to $c(\text{NaOH}) = 20\%$, corresponding to the alkalization step in the technical viscose process. Here, obviously the existence of two structural fractions with different amounts of NaOH and water sorbed has to be assumed. The application of the *RSF* concept to the second step of the integral sorption isotherm at $c(\text{NaOH}) > 20\%$ is still open. This second step in the integral sorption isotherm might be caused by a change of alkali cellulose modification from Na-cellulose I to Na-cellulose II associated with an increase in the NaOH/AGU ratio in the ordered regions, and/or an increase of the disordered fraction, possibly accompanied by a change in its NaOH and water binding. Further progress in understanding the interaction between cellulose and aqueous alkali, especially at $c(\text{NaOH}) > 20\%$, can be expected from more precise sorption data in this range of high alkali concentration in connection with a deeper insight into the structure of the disordered regions of cellulose and alkali cellulose, and also by including the aspect of solvation, with respect to the existence of defined NaOH hydrates¹⁵ in the discussion and interpretation of sorption data.

Finally the applicability of the *RSF* concept to other heterogeneous reactions of cellulose might be suggested.

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