Budapest University of Technology and Economics
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Effect of Tetramethylammonium Hydroxide on Cellulose in Comparison with Sodium Hydroxide

Summary of Ph.D. Dissertation

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Introduction, the aim of the work

Cellulose is the most widely available renewable raw material, with more and more applications. In various cellulose technologies usually disruption of highly ordered supermolecular structure (activation) is needed. For this purpose commonly **aqueous solution of** sodium **hydroxide** is used: in proper concentrations it is an **intracrystalline swelling agent of cellulose.** Its technological importance was discovered and patented by John Mercer already in 1850. Since that time a large number of scientific publications have appeared on the cellulose swelling effect of sodium hydroxide.

Much less is known about the other swelling agents of cellulose. This is especially true for the **tetraalkylammonium hydroxides,** whose aqueous solutions of proper concentrations are also intracrystalline swelling agent of cellulose; **in case of large alkyl groups the swelling is unlimited, the cellulose dissolves.** The first paper on the effect of these organic bases on cellulose was published by Dehnert and König in 1925. The quaternary ammonium hydroxides, especially the one with the smallest molecule, namely **the tetramethylammonium hydroxyde (TMAH)** have other practical applications (like pyrolysis GC/MS analysis of polymers, cleaning the surface of semiconductors). These applications in the electronic industry will hopefully decrease their high prices, thus leading to other areas of applications as well.

Recently TMAH was successfully applied for the delignification of various cellulose sources (wood, annual plants) by Tánczos and Schmidt, Johannes Kepler University, Linz, Austria; their process was patented in 1998. The effect of the aqueous solution of TMAH on cellulose has not been studied in Linz, this research is performed at the Department of Plastics and Rubber Technology of the Budapest University of Technology and Economics, within the framework of a bilateral research cooperation. I became involved in this research during my graduate and postgraduate studies.

The aim of my Ph. D. studies was a better understanding of the interaction of aqueous solution of TMAH with cellulose, and the properties of cotton cellulose swollen in equilibrium. These studies have also been extended to certain properties of the swelling liquids and to some technological processes as well. Every experiment has been performed with the aqueous solution of sodium hydroxide as well, in order to evaluate the results as a comparison of the two swelling agents.

Preliminaries

At the beginning of my research it was already known that the tetraalkyl-ammonium type organic bases are more effective swelling agents of cellulose than sodium hydroxide – in case of molecular size large enough the swelling of is unlimited, the cellulose dissolves. This effect has been attributed to the large size and apolar character of the cations, supposing that they can therefore penetrate even into the apolar parts of the cellulose bonded by van der Waals forces, preventing the recombination of the cellulose chains.

It was also known that TMAH, the smallest member of the tetraalkylammonium hydroxide family, which cannot dissolve the cellulose due to its size, can more successfully been applied for pulping of various woods and annual plants, for the delignification of cellulose, than the sodium hydroxide and the tetraalkyl ammonium hydroxides of larger molecule size. This effect has been attributed to many parameters, like the significantly larger activity of the TMAH (it is nearly 50% larger than that of NaOH), the partial dissolution of the hemicelluloses which helps the separation of lignin, the increased disruption of the nonphenolic ether linkages of lignin, and the solvatation of lignin moieties.

There was almost no reference in the scientific literature about the effect of tetraalkyl ammonium hydroxides on cellulose. I supposed that the specific properties of these chemicals must also appear in the swelling process of cellulose and in the properties of the swollen fibre. Therefore I performed experiments with TMAH (which is effective in pulping) on bleached cotton fabric which is practically pure α-cellulose. Furthermore I studied some characteristics of the swelling liquids and the effectiveness of the two chemicals in certain technological processes.

Results

1. According to **computer aided calculations** in molecule modelling, the total intermolecular crystal energy is claimed **in the literature** to be 20 kcal/mol (84 kJ/mol), only 2-3 kcal/mol (8,4-12,6 kJ/mol) being attributed to the hydrogen bonds, the rest to the van der Waals bonds. I pointed out in view of these data that the apolar character of the tetraalkylammonium cations is extremely important.

2. **Characteristics of the solution:** I studied those properties of the solutions of NaOH and TMAH which may directly or indirectly be related to the penetration of liquids into cellulose (density, viscosity, surface tension, conductivity).

a) **Surface tension (γ):** NaOH is capillary inactive, the surface tension of its aqueous solution slightly increases as a function of the concentration, while that of the capillary active TMAH greatly decreases.

b) **Density (ρ), viscosity (η):** In the case of solutions of identical concentration density of NaOH is larger than that of TMAH (at 3 mol/dm^3 – NaOH: 1,1073 g/cm^3, TMAH: 1,0194 g/cm^3); viscosity of both types of solution is increasing with increasing concentration, especially that of TMAH (at 2,8 mol/dm^3 – NaOH: 1,5386 mPas, TMAH: 2,7624 mPas). Based on the density data it can be supposed that the free volume is large in the TMAH solution, hence the large viscosity may rather be attributed to the large energy demand of hole formation and that of detachment of TMAH molecules from neighbours.

c) **Conductivity:** The conductivity of both strong electrolytes increases as a function of concentration. By modifying the model, originally developed for smaller concentrations, this function can be described up to 2 mol/kg water concentration. In this concentration the conductivity of TMAH solution differs significantly stronger from the ideal value of the diluted solutions, than that of the NaOH solution.

Comparing those properties of the solutions which directly influence the penetration into the pores of the fibre I found that the ratio $\gamma*\eta/\rho$ is practically the same:

$\gamma_{TMAH}*\eta_{TMAH}/\rho_{TMAH}$: $\gamma_{NaOH}*\eta_{NaOH}/\rho_{NaOH}$ ratio 0,96 (c= 2,8 mol/dm^3).

3. **A complex description of the cellulose–swelling agent interaction has been obtained.** Even in case of NaOH no complex research has been published with the aim of presenting the process of cellulose swelling using all the methods of my work for the same substrate.

a) **Wetting:** The short time of the penetration of the liquid into the cellulose and the swelling of the cellulose makes the measurement of the contact angle difficult. The order of the measured contact angles is: $\theta_{water}<\theta_{3MNaOH}<\theta_{3MTMAH}<\theta_{6MNaOH}$. In spite of the capillary activity of the liquid, the initial contact angle of the TMAH is greater than that of the water, due to the positive adsorption of the cations. The large contact angle of the highly concentrated NaOH solution is caused by the high ionic strength.

b) **Preferential sorption:** The measured data are the consequence of the sorptions both of the water and the bases; the adsorption isotherms, as obtained on the cellulose in the above way, are identical, as it has already been described for NaOH and tetraethylammonium hydroxide. The S shape of the isotherm can be due to the fact that during the swelling new surfaces are deliberated.

c) **Heat of immersion:** The heat measured during immersion of cellulose into the aqueous solution of swelling agent is derived from the heat effects of swelling (endotherm) and adsorption (exotherm); the S-shaped curve of concentration dependence is similar to the change of various parameters characterising the degree of mercerisation in the literature; the heat of immersion in TMAH solution is slightly, but significantly smaller than that measured in case of NaOH; they become identical (~75 J/g) at 2,8 mol/dm^3 concentration.

d) **Retention of swelling agents:** Due to the higher degree of swelling samples retain more TMAH solution than NaOH solution after centrifugation (at 3 mol/dm^3 NaOH: 85 %, TMAH: 110 %).

e) **Pyrolysis:** The temperature of the initial decomposition of cotton cellulose decreased from 350 °C to ~250 °C in the case of NaOH and to 230 °C in the case of TMAH. Decomposition of TMAH cannot be detected on cellulose at 134 °C, probably due to development of the more stable tetramethylammonium cellulosate.

Summarising the results obtained from the study of cellulose–swelling agent interaction it can be concluded that the TMAH solution has significantly larger effect on the cellulose than the NaOH solution according to the data of wetting and retention of swelling solutions, while there is almost no difference (if any) in the data of preferential sorption of bases and heat of immersion. These latters are results of two processes of opposite directions; I did not study the possible differences in the partial processes.

4. **The properties of the cellulose swollen in equilibrium** have been changed at all the three structural levels (molecular, supermolecular and morphology) as expected. The macroscopic characteristics have also changed at the same time.

a) Molecular change

Degradation: Degree of polymerisation has been decreased by TMAH to a larger extent than by NaOH; the greater degradation effect of TMAH can be seen in data of weight loss (NaOH: 0,59 %, TMAH: 1,21 %) and in the absorbance of the product of decomposition (NaOH: 0,118, TMAH: 0,315) as well.

b) Supermolecular structure

Crystallinity: In the case of TMAH a smaller concentration (2,8 mol/dm^3) is needed for the Cellulose I – Cellulose II transition than in the case of NaOH (4 mol/dm^3). In the studied range of concentration the ratio of Cellulose II changed between 0 and 16%. According to the literature applying liquid ammonia treatment before swelling with NaOH Cellulose I – Cellulose II transition occurs at lower concentration values and it becomes complete. However, my results show that the liquid ammonia pre-treatment of the cotton cellulose practically does not influence the result of the subsequent swelling effect of either chemicals.

Intermolecular hydrogen bonds, segment movement: The intensity of intermolecular hydrogen bonds decreased by growing concentration of both chemicals (FTIR), while segment movement (development of crosslinks during γ-irradiation) increased; increase of molecular disorder is more significant in TMAH treated samples, especially at concentrations > 2 mol/dm^3.

Accessibility: TMAH causes higher improvement of accessibility than NaOH. It is proved by several data: water retention values in the whole concentration range, immersion heat values of swollen samples measured in water and in swelling solutions (same as it was used for pretreatment), respectively, and iodine sorption capacity at concentrations > 2 mol/dm^3; at 2,8 mol/dm^3 concentration these values for TMAH treated samples are significantly higher than those of NaOH treated ones (water retention – NaOH: 44 %, TMAH: 80 %, heat of immersion in water – NaOH: 50 J/g, TMAH: 55 J/g, heat of immersion in swelling solution – NaOH: 63 J/g, TMAH: 80 J/g, iodine sorption capacity NaOH: 43 mg iodine/g cellulose, TMAH: 50 mg iodine/g cellulose).

c) Morphology

Specific area/porosity: BET-surface and porosity measured by nitrogen adsorption of TMAH treated cellulose are higher than those of NaOH treated samples (at 3 mol/dm^3 – NaOH: 178 m^2/g, TMAH: 191 m^2/g, and NaOH: 0,2242 cm^3/g, TMAH: 0,2591 cm^3/g, respectively). Fibre diameter is increased by swelling, deconvolution of fibre occurs. At 3 mol/dm^3 concentration, the degree of convolution of the TMAH treated fibre is much higher than that of the untreated one. Similar phenomenon has not been occurred in the case of any other swelling agent. It can be supposed that the apolar character of TMAH and the high degree of aggregation of fibrils have significant role in the extreme convolution.

d) Macroscopic characteristics

The cotton fabric is shrinking during swelling (max. ~ 30 %). Degree of shrinking, mass of unit area and tensile strength are changing along an S-shaped curve with growing concentration, the effects of 3 mol/dm^3 TMAH and 6 mol/dm^3 NaOH are nearly same.

Summarising: TMAH is a more effective swelling agent of the cellulose than NaOH, as shown by the changes in all the three structural levels of the cellulose and by the macro-characteristics as well. There are a few exceptions (inter- and intramolecular hydrogen bonds, immersion heats of swollen cellulose measured in water and in swelling solutions, iodine sorption capacity) in the concentration range of less than 2 mol/dm^3; this latter phenomena may be attributed to the large size of the hydrated ion pair of TMAH.

5. **During the technological applications TMAH proved to be more effective than NaOH** in delignification of hemp, scouring of cotton, and mercerisation, respectively Nevertheless, substitution of the cheap NaOH by TMAH cannot be suggested, further research is still needed and further conditions (like the regeneration of TMAH) are to be satisfied. The application of TMAH and the proof of its efficiency in these theoretically well-known processes wished to emphasise the difference between these two swelling agent.

MAIN RESULTS

1. I discovered that the previously published results of certain computer-aided molecule-modelling calculations are in strong connection with the special swelling effect of the apolar quaternary ammonium cations: according to calculations only 10-15 % of the total crystal energy is originated from hydrogen bonds which had been considered crucial before; great contribution of van der Waals forces emphasises the importance of apolar character of quaternary ammonium cations in the swelling process.

2. I determined the concentration dependence of cellulose swelling effect of NaOH and TMAH: in the concentration range larger than about 2 mol/ dm^3 TMAH is a more effective swelling agent of the cellulose than NaOH. According to data of many characteristics TMAH was as effective at 3 mol/dm^3 concentration as NaOH was at 6 mol/dm^3 concentration. This was shown by the results of water retention, BET-surface, shrinking, tensile strength, elongation, and dye adsorption.

3. I found that the penetrations of 3 mol/dm^3 TMAH and 6 mol/dm^3 NaOH into cellulose are hindered due to the small wetting ability of the solutions and to the narrowing of the pores of the cellulose.

4. I suggested to use the degree of crosslinking developed during high energy irradiation for the characterisation of segment movement.

5. Evaluating microscopic pictures I found fibre swollen in 3 mol/dm^3 TMAH more convoluted than the untreated one.

6. Tetramethylammonium hydroxide is more effective in some technologies (delignification of hemp, scouring of cotton, mercerisation) than NaOH.

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Papers

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Radiation Physics and Chemistry 67, 509-512 (2003)

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10th 'Tihany' Symposium on Radiation Chemistry, Sopron (P-36), (2002)

3. T. Tóth, J. Borsa, E. Takács, I. Sajó: Effect of preswelling on radiation degradation of cotton cellulose
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