Model for water in paper

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Abstract

In this article an attempt is made to make an useful describtion of the behaviour of water in paper.

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1 Introduction

There are two usual ways to describe the behaviour of water in paper, and other fiber materials. The first way is to mould it into the form of standard thermodynamics describtion which leads to a number of not very clear parameters, which certainly give not a very good picture of what is really happening inside the paper material. The other way is to apply statistics, to work from a view of binding probability between water molecule with water molecule and water molecule with hydroxygroup of a glucose molecule in the paper. This method is quite difficult and usually not extended beyond the basic results. In this paper a attempt is made to combine the two ideas to practical, as well as visualising, model for the behaviour of water molecules in paper.

The demand for such a model comes from the conservation science because detoriation and coloration of paper might have more to do with water than water as component in oxidation reaction and water as solvent. At very high water concentrations the transport properties of water are well established, but at " low " concentrations the water content is still considerable and it effects shouldn't be overlooked. Temperature changes and humidity changes can pump enormous amounts of energy in the paper, which don't come out when it is changed back. This gives the typical hysteresis shape. Where goes that energy, how is it dissipated?

This article does not pretend to answer all questions, but gives hints in which direction, the author

thinks, some answers may be found.

2 Theory

2.1 Thermodynamics

The only thermodynamical quantities which are useful here and have clear physical meaning are temperature (T), watervapor pressure (P), and the humidity (n) which is the fraction of the maximum water pressure, or saturation pressure, at the given temperature.

At every given humidity there is water in paper at equilibrium. That means that water binds to paper more easy than that it condensates. In terms of thermodynamics there is more energy needed to vaporize this water, which leads some people to conclude that the water is frozen into the paper. The amount of energy is equal to the energy released by expansion of the gas.

$$E \;=\; \int_{P_i}^{P_f} P dV \;=\; \int_{nP_{sat}}^{P_{sat}} \frac{RT}{P} dP \;=\; -RT ln[n] \tag{1}$$

This by virtue of the ideal gas law.

2.2 One layer

Now it is useful to find the the occupation probability of hydroxy sites in the paper, by water molecules. This depends on the chance that a molecule is near the site, which is proportional to the number of molecules present in a volume, so proportional with $\frac{P}{RT}$. It is also proportional to the statistical probability of binding for which Boltzmann's law gives a good estimate $e^{\frac{E_{binding}}{RT}} \propto \frac{N_w^{bound}}{N_w^{free}}$. The number of molecules that binds is also proportional to the number of available sites, which in it's turn is proportional to the weight of the paper (and the type). Let's say N_s sites per kilogram paper. So to put it all together we get:

$$N_w^{bound} = Q \ (N_s - N_w^{bound}) e^{\frac{E_{binding}}{RT}} N_w^{free} \frac{P}{RT} \tag{2}$$

Where Q the general proportional factor, now it more practical to express N_w^{free} in the pressure which is basically the same quantity.

$$N_w^{free} \propto \frac{P}{RT} \tag{3}$$

Now it is possible to express the number of binding molecules in terms of known quantities and an unkown Q which now changes value.

$$N_w^{bound} = \frac{N_s}{((Qe^{-E_b/RT}(RT)^\alpha/P^\alpha) - 1)} \tag{4}$$

With α is 2. This looks similar to Langmuir one layer equation. The difference is the second factor P/RT. One might wonder about this. The first term came from the number of molecules present in the vincinity of a hydroxygroup. A higher number gives rise to a higher binding probability. The second one came from temperature dependency, if a molecule is near enough to bind what is the chance that it actually will bind. The latter is a bit controversial because one can argue that if a molecule has the possibility to bind it will always bind. So one might take α 1 or 2. The exponential factor is left there because one must expect a temperature dependency. This is then at the same time a test for what is happening.

2.3 Other water

Now there is one layer of water bound to the paper. This binding is quite strong so it looks more icy than watery, other water molecules can profit from that. It is like watervapor condensates on ice to make an equilibrium. The first layer was a statistical layer this means that thermodynamical equilibrium is not required,(?!) one can well imagine that a watermolecule which spend most time bound to a hydroxygroup has a lower than thermal energy (kinetical, rotational or vibrational modes). This makes possible to have thermal equilibrium where other molecules have on the average more energy than thermodynamically allowed.

The amount of energy available is proportional to the number of bound molecules and can further only depend on the temperature.

This model is based on a few assumptions. That is that the present of extra water does not create a more favorable climate for binding of water molecules to paper, and that water on paper looks to other water molecules like watermolecules bound to water molecule clusters. The first assumption might look acceptable if one sees the water paper boundary as a fixed boundary similar as a water air boundary, molecules cross that boundary from one surrounding to the other, and adhesiveness is explicitly (!) build in. The other assumption looks realistic if one realises that the binding force between water molecule and the hydroxygroup of the paper is of the same order of magnitude as the water molecule water molecule hydrogenbond, then it looks like the paper plus bounded water is one big water cluster. So now the bounded water statistical system and the extra water thermodynamical system is separated that means there are certain statistical characteristics for the bounded water which by virtue of that part of the model only depends on temperature and water vapor pressure. That means that per bounded water molecule there is δE energy available to diffuse around it.

2.4 The total system

There is $\delta E \ N_w^{bound}$ energy available, so at a given humidity then $N_w^{extra} = -N_w^{bound} \delta E / RT ln(n)$ is the extra water which can profit. The only thing now needed to be able to express the water content in paper is the value of δE. For now we are satisfied with a parameter with the right dependency on other parameters, which is in this case only the temperature. The factor $e^{\frac{-E_{binding}}{RT}}$ gives the binding chance so gives also a good estimate for the time the water molecule spend bound to the hydroxy group before it loosenes. The possibility to mixes with the other water is the reciprocal of that value.

$$\delta E(T) \ = \ \delta E e^{\frac{E_{binding}}{RT}} \tag{5}$$

That gives a total equation for the water content of paper.

$$N_w^{paper} \ = \ N_w^{bound} \left(1 \ + \ \frac{\delta E e^{E_{binding}/RT}}{-RT \ ln(n)} \right) \tag{6}$$

Using the expression we have for N_w^{bound}, we get.

$$N_w^{paper} \ = \ \frac{N_s}{Q e^{\frac{-E_{binding}}{RT}} (\frac{RT}{P})^\alpha - 1} \left(1 \ + \ \frac{\delta E e^{E_{binding}/RT}}{-RT \ ln(n)} \right) \tag{7}$$

There are only two parameters left in the model, those are Q and δE, for the latter it is possible to make an estimate because effective it is the leftover of what an only water model would give so $0 < \delta E < E_{binding} - \frac{1}{2} E_{hydrogenbond} \approx \frac{1}{2} E_{hydrogenbond}$. The pressure P can be expressed with use of Clausius-Clapeyron equation in terms of humidity, latent evaporation heat L and temperature.

$$P = n P_0 e^{(\frac{L}{R})(\frac{1}{T_0} - \frac{1}{T})} \tag{8}$$

There are some problems with finding the right value for N_s, that is the number of available sites because some sites are in difficult penetrable areas like crystalline cellulose. But that will only be a small correction upon the whole number. A more important factor to take in account is the physical density of the paper because if there is no space for more water then no more water will go into the paper. This makes that the relative water content in wood diverts only at high relative humidities from the water content in paper, if it is corrected for the present of other substances. The other factor in the physical limitations is that when a lot of water is present the range of effect of the bound water may be to small to reach all water, then we have to fall back on surface tension formulaes which are valid in this region.

3 Flow

If water is present the water vapor flow is usually not taken in account. But now we have a system which has in a specific way the whole range of flow types, from water type flow, that is the flow where water pressure pushes the the bulk water forward, to the water vapor flow which is diffusion type where the density gradient determines the flow. One can imagines that the paper fibers are reservoirs for water, if one changes the conditions the reservoirs have to be filled or emptied, so the propagation of the change is slowed down, or if the gaslike part of the condition was able to follow the change and the waterlike wasn't able, there exists a local non equilibrium. So will energy be pumped into the paper irreversible, and because the water content in paper is considerable this can be a big amount.
If the latter is not taken in account it is possible to write down a flow differential equation. This one is highly non linear and exhibits an dissipative term because at an increasing watercontent the water binding to the paper has a higher energy then at a decreasing watercontent it's loosening energy. If it was only statistical effect the it would be linear with the speed in which the system is changed. If one has a watertype flow one can also some type of friction between the bound water and the extra water which has an quadratic energy dissipation dependent on the change rate. The microscopical and macroscopical deformation energy dissipation are independent of the speed in wich the system changes.
Transport phenomena depends only on the water type flow, but because this has a whole range behaviour the transported object sizes and characteristics determines the transport speed. One must realize that here for transport the same two types are possible, the object is dragged along with the water flow and the object takes a stochastic path in the water.

$$dissipation = deformation\ dissipation + rate \times statistical\ dissipation +$$

$$(rate)^2 \times frictional\ dissipation \tag{9}$$

4 Microsopic energy dissipation

Apart from the basic model which gives good results, it's effects might be obscure because it does not include real microscopic behaviour. The microscopic background is not easy because it asks for a method which lies between the quantum mechanical and the classical treatment. Different models for binding reactions still give different results depending, for instance, on the way nuclear motion is included. The possible quantummechanical states the molecule can be in depends on the energy levels of, for instance, vibrational modes. If we assume local abiabatic behaviour, that is local energy conservation, then the energy will be released in quanta of the same of energy amount as the binding energy and energy levels of modes. This gives a small bump or hole in the Planck energy spectrum which will disappear fast be internal conversion, this will give a higher temperature.

5 Appendices

5.1 Appendix A flow

If we want to right down an flow equation we have to use a field that is unambigious over the whole range. The gas pressure in the areas between the fibers is a good candidate. The steady flow equation is relatively easy then because it does not contain a time dependency.

$$\nabla \cdot \lambda \nabla f(P) = 0 \tag{10}$$

Where ∇ is the gradient operator $(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$ and f(P) a injective function of the watervapor pressure P. It is possible to measure an one dimensional steady flow pressure curve and gain by inversion the f(P). The λ is a diagonal matrix wich contains the information on the fiber structure, it is so to say the square of the mean pathlength a water molecule has to take get from A to B, two points at unit distance along one of the axis. With an electron microscope it is good possible to make an estimate for this matrix, at low vapor pressure. But one might expect an dependency on f(P) because with the changing pressure the whole nature of the behaviour of the water molecules changes. The expression can be further simplified.

$$\nabla f(P) = \frac{\partial f(P)}{\partial P} \nabla P \tag{11}$$

Substituting this in the orginal equation gives.

$$(\frac{\partial^2 f(P)}{\partial P^2})[\nabla P] \cdot [\lambda \nabla P] + \frac{\partial f(P)}{\partial P}[\nabla \cdot [\lambda] \nabla P] + (\frac{\partial f(P)}{\partial P}) \left(\frac{\partial \lambda}{\partial P} \right) [\nabla P] \cdot [\nabla P] = 0 \tag{12}$$

The ∇ does not work on ∇ any more. The last term can create an extra dissipative behaviour, especially at higher humidities. And it is structure dependent(!). The normal dissipation is equal to the flow rate multiplied with the energy released through expansion of the gas, which is $RTln(\frac{P_i}{P_f})$. To describe the time dependent flow, one must make a much bigger effort for an equation which is probably not solveable. So we leave that.
But the shape must be something like.

$$\nabla \cdot \lambda \nabla f(P) = \int_{-\infty}^{t} g(P(t'))dt' \tag{13}$$

Where f(P) is also an weighted integral over t.
The thing now needed are the explicit functions f(P) and $\lambda(P)$. Or even better $\lambda(f(P))$ which keep the differential equations more simple. If the water in paper is separated in the three different types of water, namely bound water, extra water and vapor, it is possible to make assumptions on the behaviour of those types separately and multiply this by the amount present at a specific pressure, and so give the right equations. This all is very well possible, but the lack of good flow measurements makes it all, at this stage, rather suggestive.

5.2 Appendix B Oxidation

The oxidation in paper is the major cause for detoriation, but oxidation is a whole set of reactions which mainly causes the depolymerisation of the long glucose chain.

5.3 Appendix C Fibers

Paper consists of long flattened fibers, about 5 μ height 25 μ width.