



# On the role of hydrogen bonding on water absorption in polymers

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## ABSTRACT

A kinetic model is proposed for the absorption of water in polymers. The process of bonding-debonding water molecules is described by two opposite reactions with different rate constants, and the key role of the concentration of traps by hydrogen bonding in the polymer matrix is highlighted. These three parameters are combined such that an equation is obtained that generalizes the model proposed by Carter and Kibler, with an additional, crossed, term. Numerical application is performed for the diffusion-absorption of water in a plane polymer sheet, and the parameter ranges where a quasi-Fickian water uptake curve is obtained are defined. The associated apparent diffusivity is shown to obey a hyperbolic variation with equilibrium water uptake for homologous series of polymers, which is in agreement with previous experimental observations.

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## 1. Introduction

The absorption of water by a polymer sample results from a sequence of two distinct processes: water dissolution in a superficial polymer layer, which can be considered as almost instantaneous, and water diffusion into the sample core, which is driven by the gradient of chemical potential.

First, let us consider water solubility. A first type of theories on the relationship between structure and solubility links the capability of a polymer to absorb water to its free volume content [1,2]. This is consistent with the fact that the crystalline phase does not absorb water in a semi-crystalline polymer, but many free-volume rich substances absorb very small amounts of water, like apolar liquids or elastomers for instance. A way to reconcile these observations is to consider that free volume is needed for water diffusion, but does not play a role in solubility. A second kind of theories [3,4] involves the role of polar groups that can establish relatively strong hydrogen bonds with water molecules. This is supported, in particular, by a wide survey of water solubility values that allows to distinguish four polymer families: family A (polymers with low polarity, e.g., hydrocarbon polymers such as polyethylene, polypropylene, polystyrene, halogenated polymers such as polytetrafluorethylene, poly(vinylidene fluoride), poly(vinyl chloride), polyalkylsiloxanes, etc.), family B (moderately polar polymers such as poly(ethylene terephthalate), bisphenol A polycarbonate,

poly(methyl methacrylate), polyamide 11, polysulfones, etc.), family C (polar polymers such as polyetherimides, etc.), and family D (polymers with high concentrations of polar groups able to act as hydrogen donors in hydrogen bonds, such as polyamide 6, amine crosslinked epoxies of high alcohol content, etc.). The order of magnitude of water uptake mass fraction at equilibrium is below 0.3% for family A, between 0.3 and 2% for family B, between 2 and 5% for family C, and above 5% for family D. Another evidence favoring this second type of theories results from the quantitative analysis of water equilibrium concentrations in families of polymers that differ only by their concentration of a given polar group, for instance polyesters for ester groups [5], polysulfones for sulfone groups [6], or amine cured epoxies for alcohol groups [7]. In all these families, the water equilibrium concentration increases regularly with the concentration of polar groups. This trend led Van Krevelen and Hoftyzer [3] to assume that water absorption is a molar additive property, i.e., that each elementary group  $i$  in the polymer is characterized by its molar contribution  $H_i$  to water equilibrium content, with  $H_i$  independent of the polymer structure. The molar equilibrium water content  $H$  in a given constituent repeat unit (CRU) would then simply be the sum of the  $H_i$ s found in the CRU. Typical orders of magnitude of  $H_i$  at saturation are less than 0.01 mol water per mole CRU for hydrocarbon and halogenated groups, about 0.1 for such polar groups as ethers, ketones or esters, which are unable to establish hydrogen bonds with themselves, and between 1 and 2 for such groups as alcohols, acids or amides able to act as hydrogen donors in hydrogen bonds. The quantitative relationship between polymer structure and water

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solubility is probably more complex than a mere molar additive rule [6,7] but, no doubt, water solubility is closely related to the content of polar groups in the polymer and to the strength of the hydrogen bonds that they are able to establish with water molecules. Not all polar sites are able to establish a complex with a water molecule, and only those able to give a complex will be considered in what follows; these active sites will be called “traps”.

Now, let us consider water diffusion. Its relationship with polymer structure has been investigated much less than for solubility. As mentioned above, diffusion needs free volume to operate, but it also depends on polymer-water interactions, as was first observed in the case of polyethylene [8] and for several polymer families afterwards, for which a quasi-hyperbolic relationship was found between diffusivity and water equilibrium concentration at saturation [9]. This result is consistent with the assumption that the bonds between traps and water molecules hinder water diffusion.

Therefore, according to the above set of observations, two kinds of water molecules coexist in a polymer sample exposed to a wet environment: mobile (free) molecules diffusing through the sample and bound (immobile) molecules temporarily delayed at traps by hydrogen bonds. This work will be limited to the case where free molecules can be captured at vacant traps only (no cluster formation) and, indeed, bound molecules can be released by the decomposition of polymer-water complexes. Therefore, the trajectory of a water molecule through a sample can be depicted as a series of random flights from one trap to another, with more or less long waiting times at these polar sites. Therefore, the global diffusion rate is expected to be a decreasing function of the concentration of traps and of the strength of polymer-water bonds.

Concerning the ratio between the concentrations of free water and bound water at equilibrium, a first indication can be derived from the study of homologous polymer series containing a single type of polar group, for instance sulfones in aromatic polysulfones as studied by Gaudichet-Maurin et al. [6]. These polymers can be described as matrices with low polarity containing highly polar sulfone groups whose volume fraction is relatively small. There is no reason to assume that the solubility and diffusivity of free water in these matrices vary strongly from one polysulfone to another. Bisphenol A polycarbonate, in which the unique polar group is an ester of low contribution to water absorption [8] is supposed to have water absorption properties close to those of aromatic polysulfones matrices. According to Table 1, the concentration of free water in these polymers would be less than 0.54%, i.e., less (and probably considerably less) than 50% of the whole water equilibrium concentration in the polysulfones. Similar observations could be inferred from series of aliphatic polyamides, where the best model for an apolar matrix would be polyethylene in which the equilibrium mass uptake would be less than 0.01% [8] against 5–10% for polyamides of the polyamide 6 type [6]. All these data lead to assume that the mass ratio between free water and bound water at equilibrium is considerably less than unity.

Regarding now diffusion kinetics, it seems clear that a Langmuir-type model, as proposed by Carter and Kibler [10] and often used in the field of composite materials since the 80s (see for

instance [11]), is a pertinent approach. Despite that, there are numerous cases of moderately hydrophilic polymers (in which plasticization and clustering effects are negligible, so that diffusivity is not concentration dependent) for which diffusion appears Fickian in a routine analysis based on the proportionality of mass uptake with respect to the square root of time up to 50% of equilibrium value or even on a visual comparison of the experimental sorption curve with a theoretical one, as illustrated by the examples of copolyamides [12], acrylic polymers [13], amine cured epoxies [14], or polysulfones [15].

Therefore, the present paper will address the following questions:

- (i) In which conditions does a Langmuir-type absorption-diffusion process lead to a quasi-Fickian water uptake curve?
- (ii) When this applies, what is the relation between the resulting apparent diffusivity and the diffusivity of free water molecules in the polymer?
- (iii) Does this relation reflect the quasi-hyperbolic dependence with respect to the equilibrium water uptake that is observed experimentally when polymers differ only by their concentration of a given polar group [9]?

## 2. Quasi-Fickian transport in the Carter and Kibler model

Forty years ago, Carter and Kibler [10] proposed a Langmuir-type model to describe anomalous (non-Fickian) diffusion of water in polymers, where trapped and mobile water molecules were accounted for. Introducing a probability per unit time  $\gamma$  for a mobile water molecule to bond, and a probability per unit time  $\beta$  for a trapped water molecule to unbind, the model writes the following equation to govern the evolution of the local concentration  $c_B$  of bound water (in moles per unit polymer mass):

$$\frac{\partial c_B}{\partial t} = \gamma c_M - \beta c_B \quad (1)$$

where  $c_M$  denotes the local concentration of mobile water. In the case of one-dimensional diffusion, as applies for instance in a plane sheet, the resulting balance of water molecules in a volume element writes as

$$D \frac{\partial^2 c_M}{\partial x^2} = \frac{\partial c_M}{\partial t} + \frac{\partial c_B}{\partial t} \quad (2)$$

where it is assumed that mobile water molecules obey Fick's law with diffusivity  $D$ .

An analytical solution was given by Carter and Kibler to the system of coupled linear differential defined by Eq. (1) and Eq. (2) in the case of an initially dry sheet of thickness  $e$  with a constant concentration of mobile water  $c_M = c_M^\infty$  prescribed on both free faces of the plate. The latter condition assumes that the ambience around the sheet is well-stirred and has a water activity unaffected by the amount of water absorbed by the specimen. The equilibrium, uniform, concentration  $c^\infty$  of water in the plate, mobile plus bound, is readily deduced from Eqs. (1) and (2):

$$\frac{c^\infty}{c_M^\infty} = 1 + \frac{\gamma}{\beta} \quad (3)$$

where  $\gamma/\beta$  is the relative contribution  $c_B^\infty/c_M^\infty$  of bound water. Note that  $\gamma$  can be positive or zero, but  $\beta$  must be strictly positive, otherwise an endless water uptake would result because trapped water molecules cannot be released. The analytical solution

**Table 1**

Concentration of sulfone groups and water equilibrium concentration in three aromatic polysulfones and in polycarbonate, according to Gaudichet-Maurin et al. [6].

Polymer	Sulfone concentration (mol/kg)	Equilibrium water mass uptake at 90% RH (%)
PSU	2.3	1.02
PPSU	2.5	1.58
PES	4.3	2.97
PC	0	0.54

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