Physico-chemical properties of edible films and coatings affected by moisture and/or flavour compounds interactions

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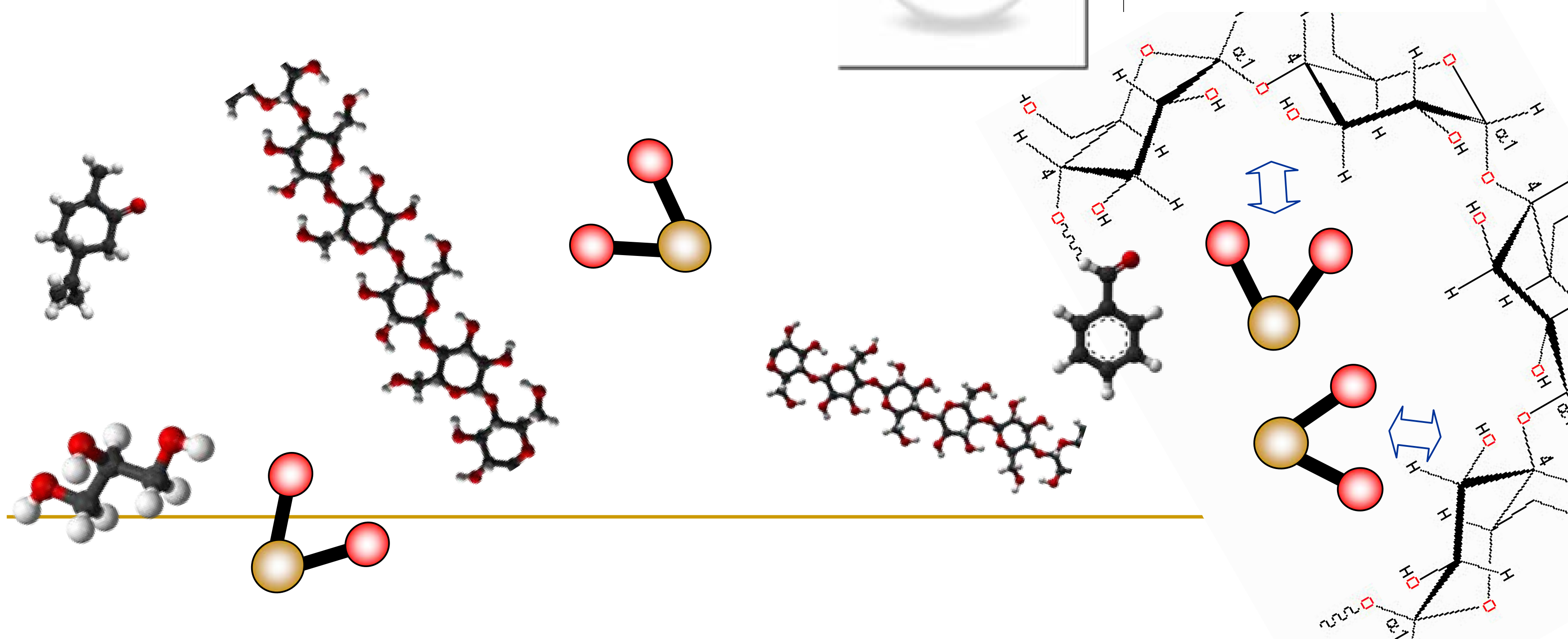


What are the solutions to prevent migrations between food compartments having different compositions or textures, or between food and surrounding medium ?

In the only case of moisture transfers :

- To obtain water activity of each compartment as close as possible

⇨ **To change recipe**

In all the cases :

To apply a barrier layer at the interface of the different compartments inside the composite food product, or at the surface of food to protect it against the surrounding medium.

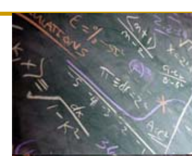
⇨ **To use edible films or coatings**

Food Industry ⇨ Predictions of shelf-life => based on diffusivity and permeability values

Modelling moisture transport phenomena (diffusivity) in food products

Model 1	Model 2	Model 3	Model 4
Assumptions			
No deformation	**simple deformation**	No deformation	**Simple deformation**
No external resistance	No external resistance	**External resistance**	**External resistance**
Eulerian coordinate x	Lagragian coordinate ξ	Eulerian coordinate x	Lagragian coordinate ξ
$D^*_{eff} = D_{eff}$	$D^*_{eff} = \frac{D_{eff}}{(1+\frac{\rho^0_{dm}}{\rho^0_x}X)^2}$	$D^*_{eff} = D_{eff}$	$D^*_{eff} = \frac{D_{eff}}{(1+\frac{\rho^0_{dm}}{\rho^0_x}X)^2}$
Boundary conditions at $x=x_{max}$ whatever the time t			
$X=X_\infty$	$X=X_\infty$	$-\rho_{dm}.D_{eff}(\frac{\partial X}{\partial x}) = ...\frac{h_m.M}{RT}(a_w p_{vsat} - p_{va})$	$\frac{-\rho^0_{dm}.D_{eff}(\frac{\partial X}{\partial \xi})}{(1+\frac{\rho^0_{dm}}{\rho^0_x}X)^2} = ...\frac{h_m.M}{RT}(a_w p_{vsat} - p_{va})$

Labuza & Hyman Trends Food Sci. Technol. 9 (1997) 47-55 - Roca et al., Food Chemistry 106 (2008) 1428–1437
Karbowiak et al., Innov. Food Sci. Emerg. Technol., 10 (2008) 116–127
Roudaut & Debeaufort in "Chemical Deterioration and Physical Instability of Food and Beverages, Woodhead pub. (2010)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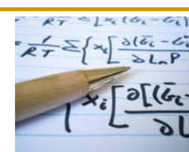

Modelling moisture transport phenomena through barrier packaging and/or edible coatings

Fick's law

stationary

$$TR = -D\frac{\partial C}{\partial x}$$

+ Henry's law

$$TR = \frac{\Delta m}{A.\Delta t} = -D.S\frac{\partial p}{\partial x} = -D.S.p^0\frac{\partial aw}{\partial x} = P.p^0\frac{\Delta aw}{L} = k.A.\Delta aw$$

transient

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

$$\frac{M_\infty - M_t}{M_\infty - M_0} = \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}exp\left[-\frac{(2n-1)^2\pi^2 D_A t}{4L_0^2}\right]$$

Shelf-life prediction

$$shelf-life \quad time = \frac{(M_C - M_i).m}{WVP.A.\Delta p}.L$$

$$shelf-life \quad time = \frac{\ln\left(\frac{M_i - M_e}{M_c - M_e}\right)}{P.A.p^0}.L.m.b$$

Based on critical content values, sorption isotherm properties, permeability RH or Aw differential, density and diffusivity, considered as constant parameters

Crank, "The Mathematics of Diffusion" (1975)
Cardoso & Labuza Food Technol. 18 (1983) 587-606
Labuza & Altunakar in "Water activity in foods : fundamentals and applications" (2007)
- Chao & Rizvi, in "Food Packaging Interactions" (1988)
- Hong et al. J. Food Proc. Preserv. 15 (1991) 45-62

Mains limits of shelf-life prediction models based on transport phenomena through barrier packaging and/or edible coatings

Are usually not considered :

Interactions between components : competitions and synergies (moisture/plasticizers/ flavours … mutual or counter diffusion)

Barrier structure changes during mass transfers (swelling, plasticization, crystallisation…)

Solvatation, partial dissolution….
(Composition and structure changes at the interface)

Shroeder Paradox (state of diffusant at inner surface),
…

As illustrated in the following slides

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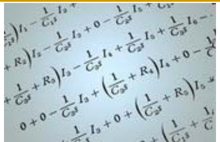
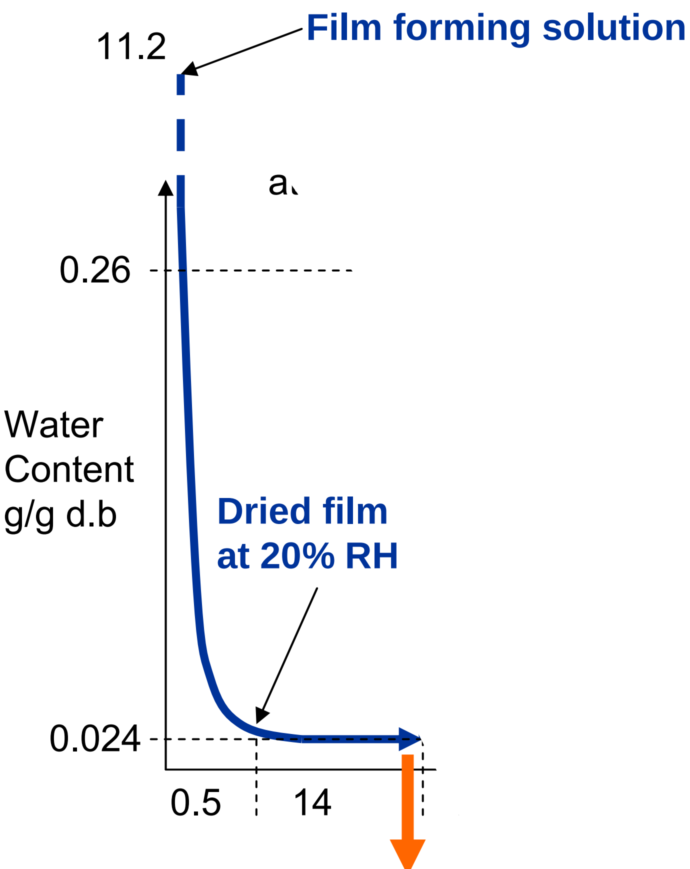
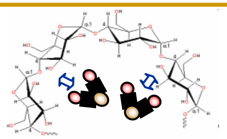


Effect of the “moisture” memory of the biopolymer (methylcellulose) structure on the water vapour permeability

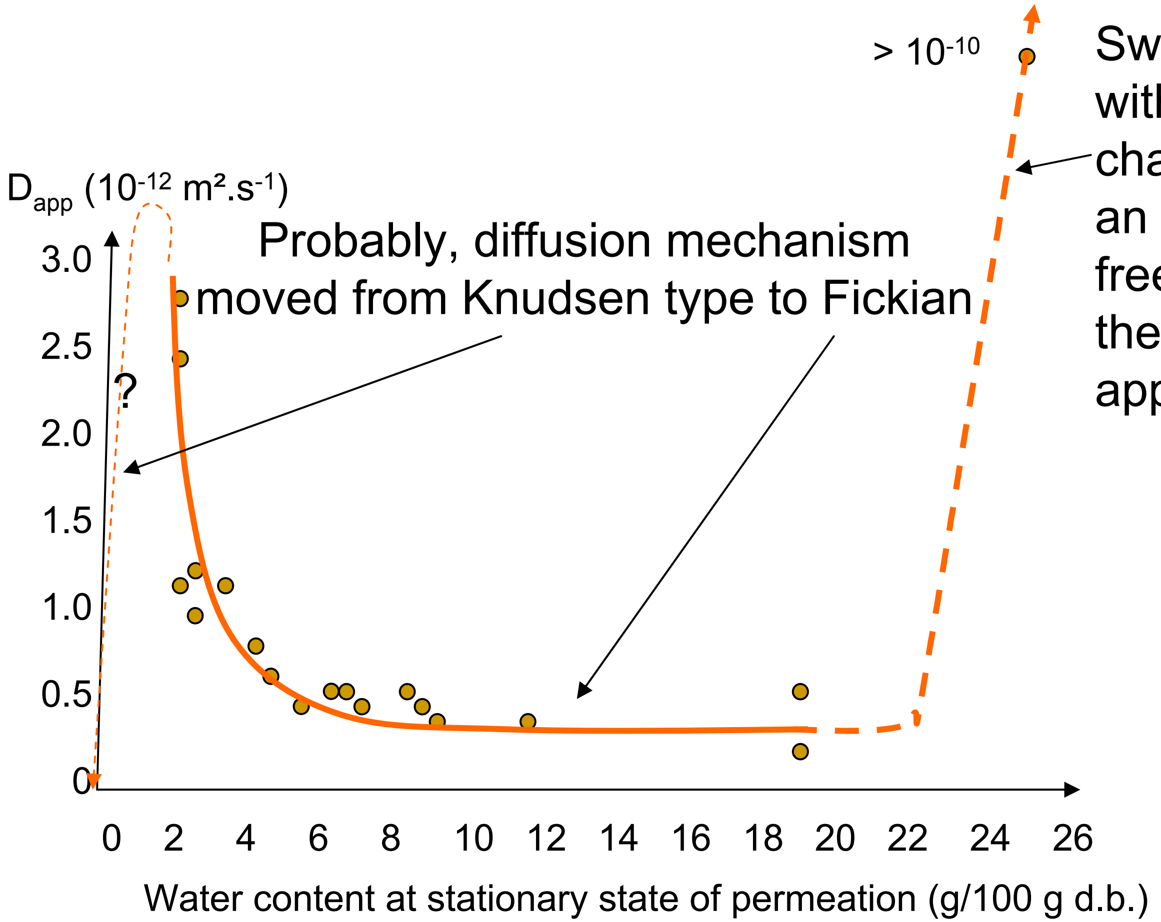


Relative permeability $P_{Rel} = 1$

Permeability increases by 13%
after rehydration
·vhile the water content at the
ary state of the
rocess was

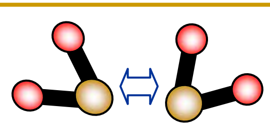


Anomalous diffusion as a function of moisture content during permeation process

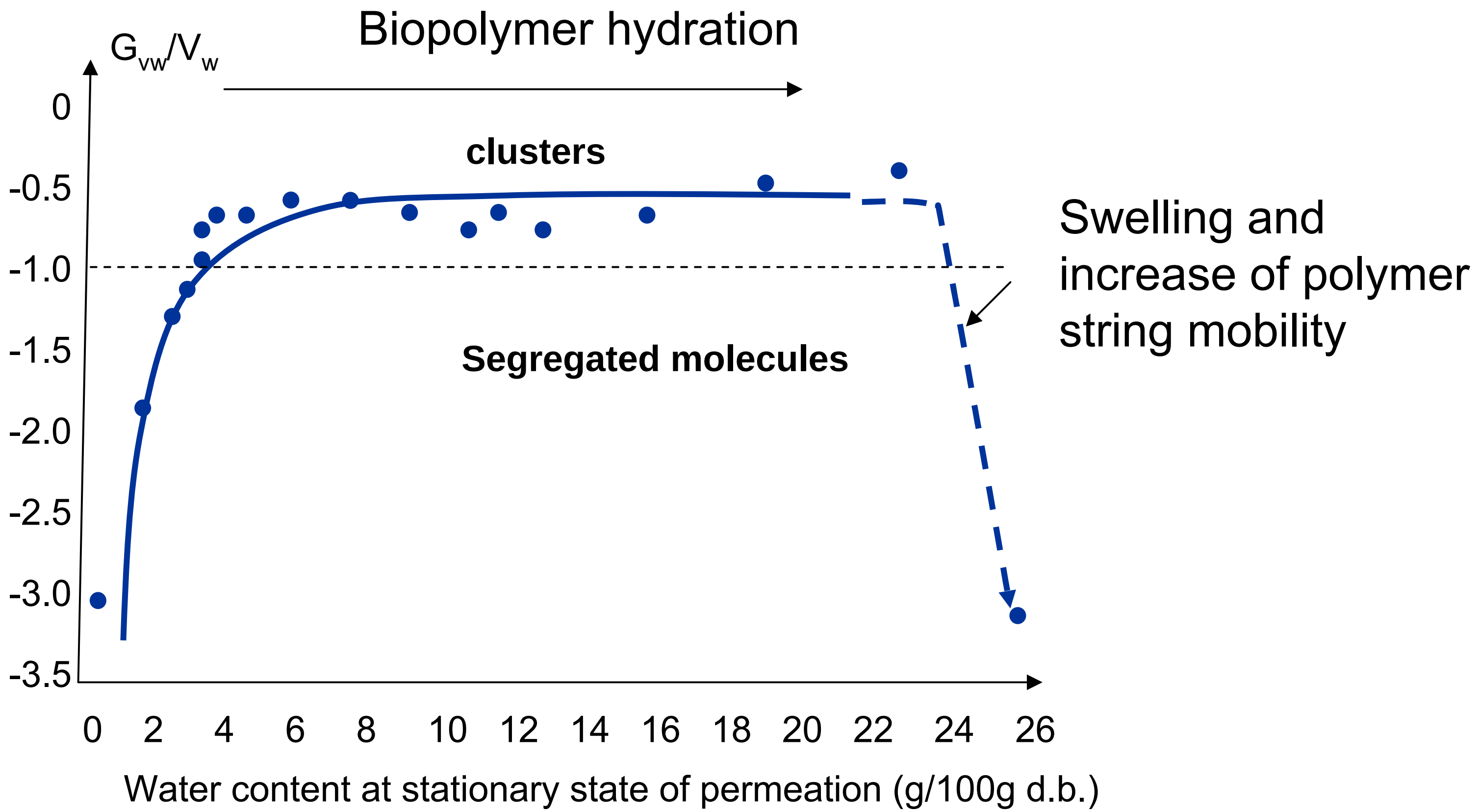


Debeaufort et al., J. Memb. Sci. 91 (1994) 125-133
Quénard & Sallée, CSTB, 323 (1991) 1-53

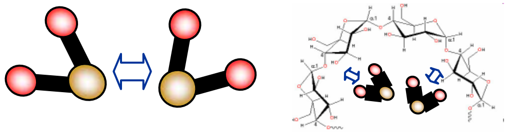
Diffusant - diffusant interactions



Anomalous diffusion caused by water-water molecule interactions within the biopolymer network stabilized by hydrophobic interactions

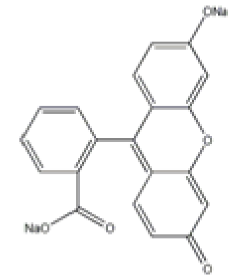


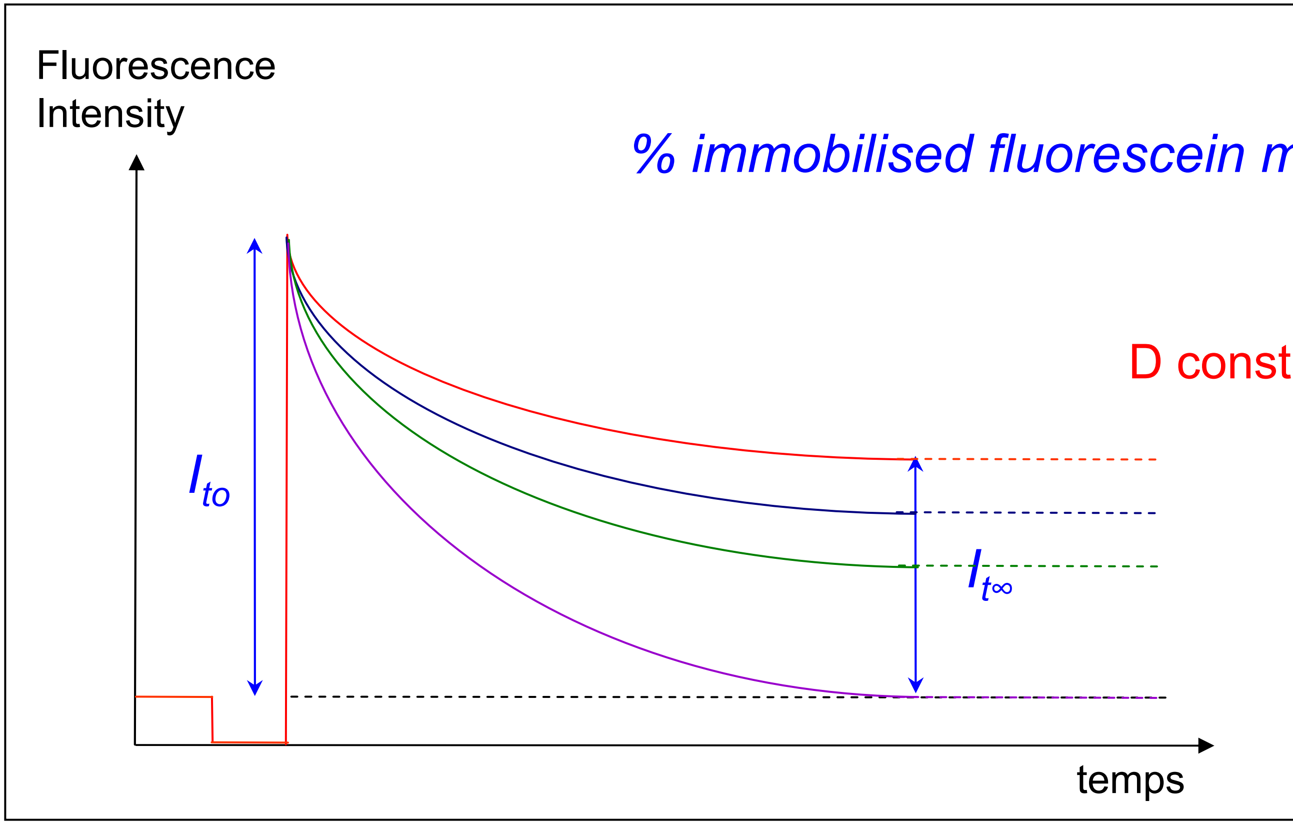
Doty, J. Chem. Phys.,14 (1946) 244-251.
Barrie in "Diffusion in Polymers", academic press, 1968
Debeaufort et al., J. Memb. Sci. 91 (1994) 125-133



Interactions between diffusant and biopolymer affect the diffusivity

Diffusivity of fluorescein in carrageenan-based edible films measured by the FRAP technique





% immobilised fluorescein molecules = $I_{t\infty} / I_{to}$

D constant

a_w < 0,7 : 50 to 60 %

a_w = 0,8 : 40 %

a_w = 0,9 : 30 %

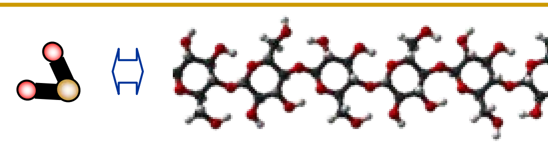
a_w = 0,98 : 0 %

D =f(H_2O)

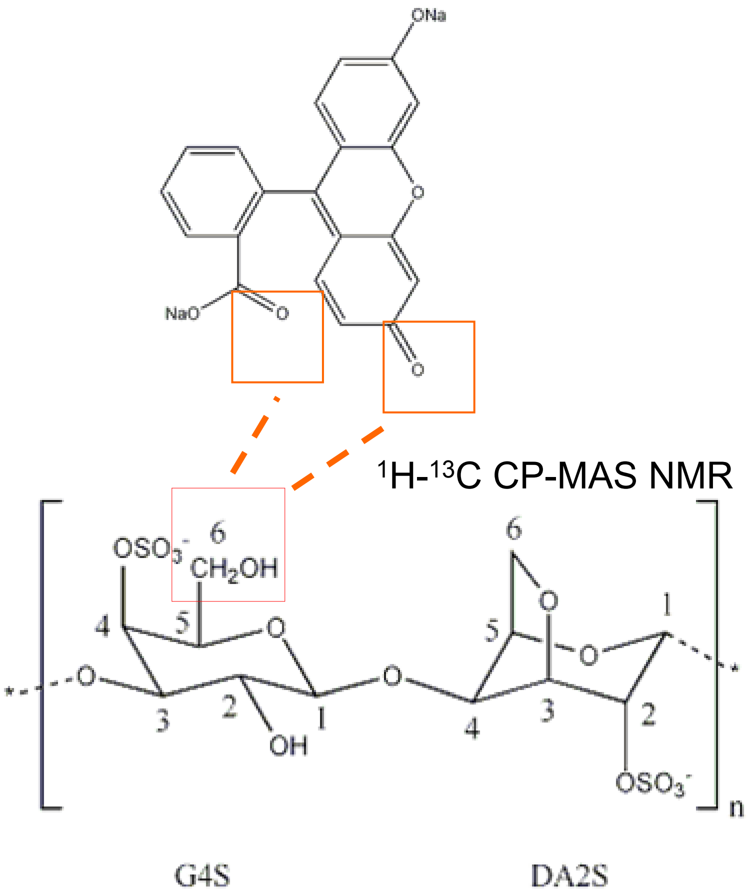
Karbowiak et al., Food Chem., 106 (2008) 1340-1349

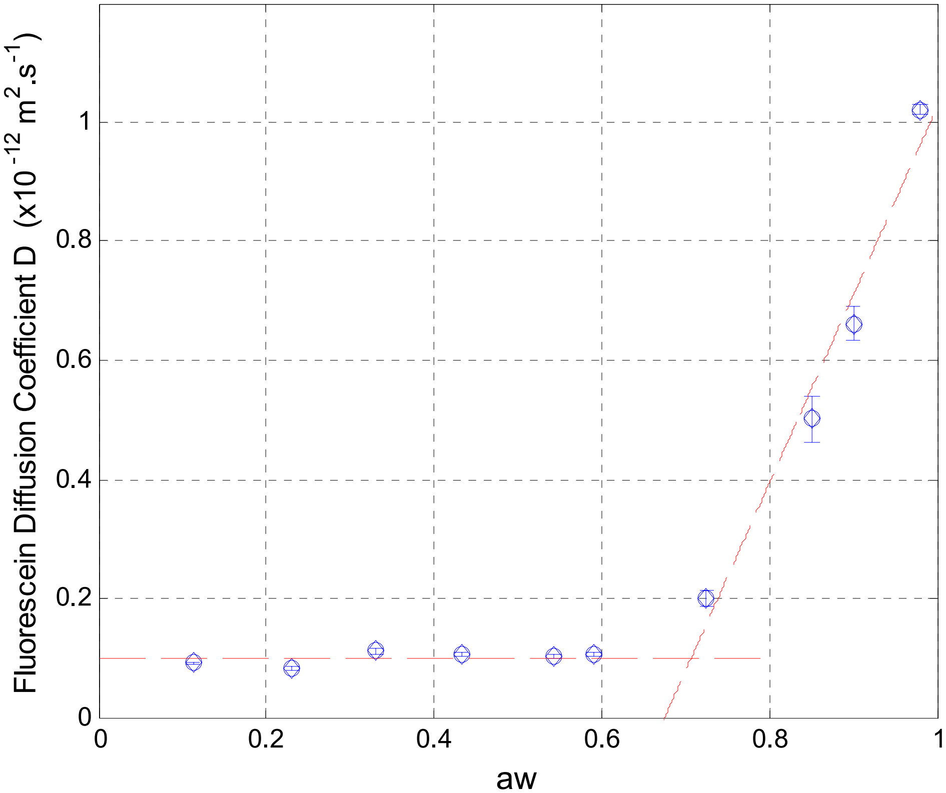
Karbowiak Innov. Food Sci. Emerg. Technol., 10 (2009) 116–127

Diffusant - biopolymer interactions

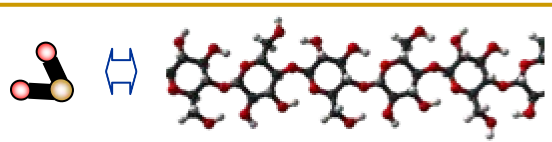


Interactions between diffusant and biopolymer affect the diffusivity less than the water content

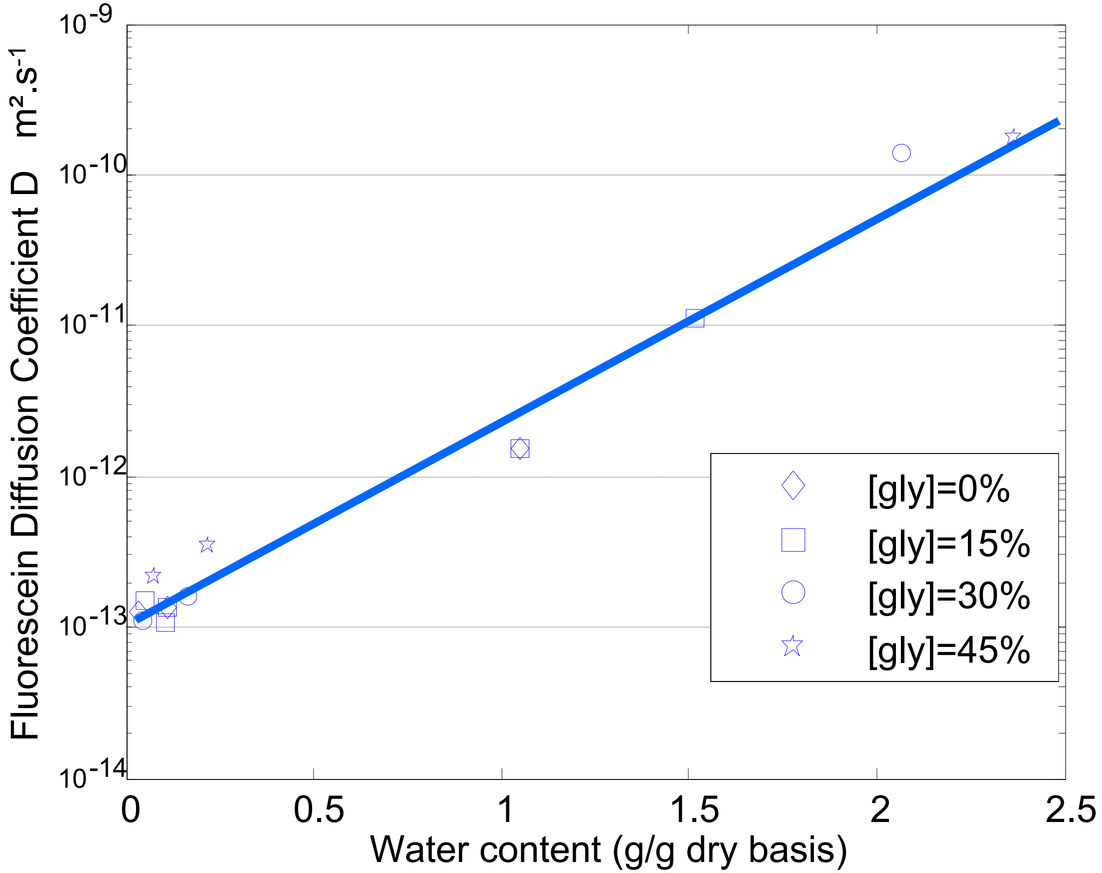




Karbowiak et al., *Food Chem.*, 106 (2008) 1340-1349
Karbowiak *Innov. Food Sci. Emerg. Technol.*, 10 (2009) 116–127



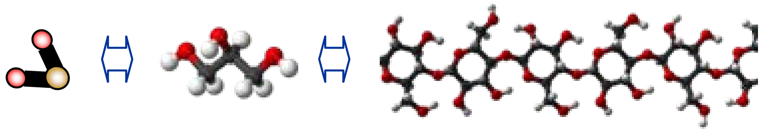
Polyol plasticizers does not affect the diffusivity of small molecules in water sensitive bio-polymers



Only the plasticizing effect of water influences the fluorescein diffusivity while the plasticizer (glycerol) varies from 0 up to 45% d.b.

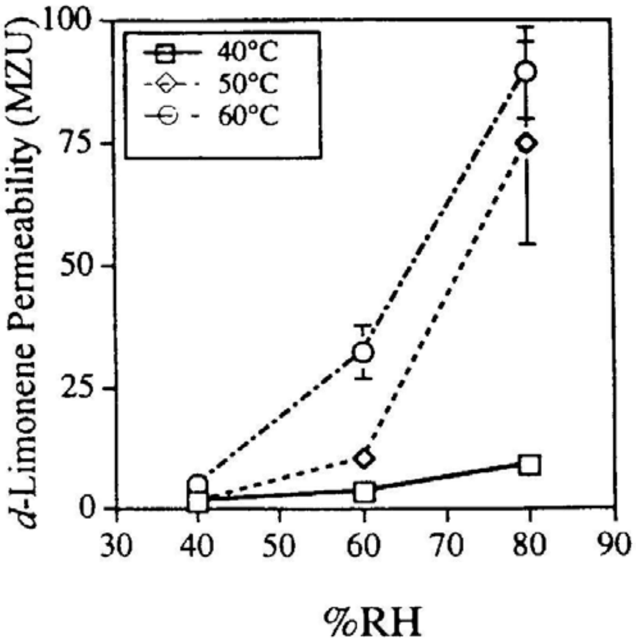
The glycerol acts as an humectant more than a plasticizer for the carrageenan-based films

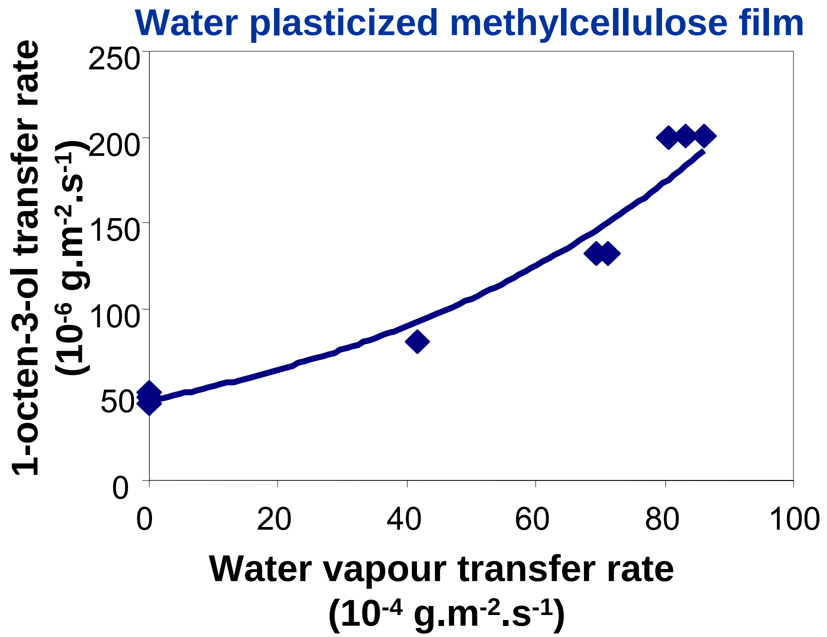
Karbowiak et al., Food Chem., 106 (2008) 1340-1349
Karbowiak Innov. Food Sci. Emerg. Technol., 10 (2009) 116–127



Water permeation favours an other diffusant (aroma) permeation through the biopolymer network

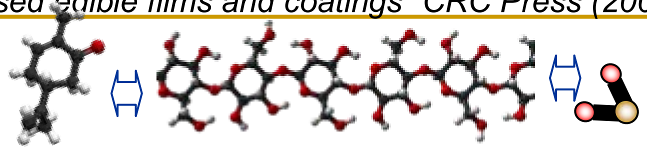
Water is a well-known and efficient plasticizer for biopolymer-based edible films



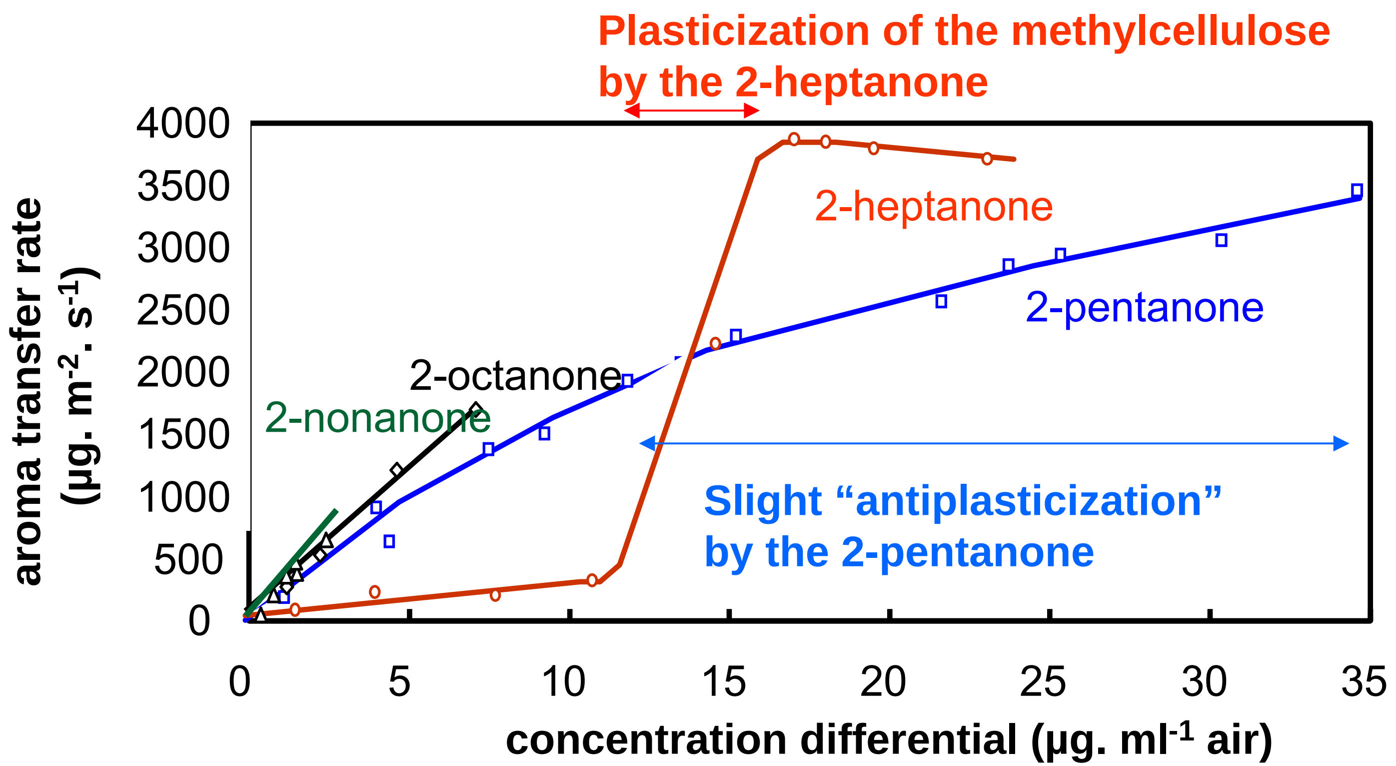


Moisture induces a swelling of the film because of a plasticization mechanism but can act as a carrier vapour when film already plasticized by water

Miller & Krochta, Trends Food Sci. & Technol., 8 (1997) 228-237
Quezada-Gallo et al., J. Agric.Food Chem. 476 (1999) 108-113
Debeaufort et al. in "Protein-based edible films and coatings" CRC Press (2002)

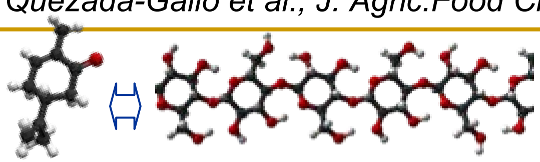


Opposite effects of methylketons (aroma) during their permeation across biopolymer (methylcellulose) network

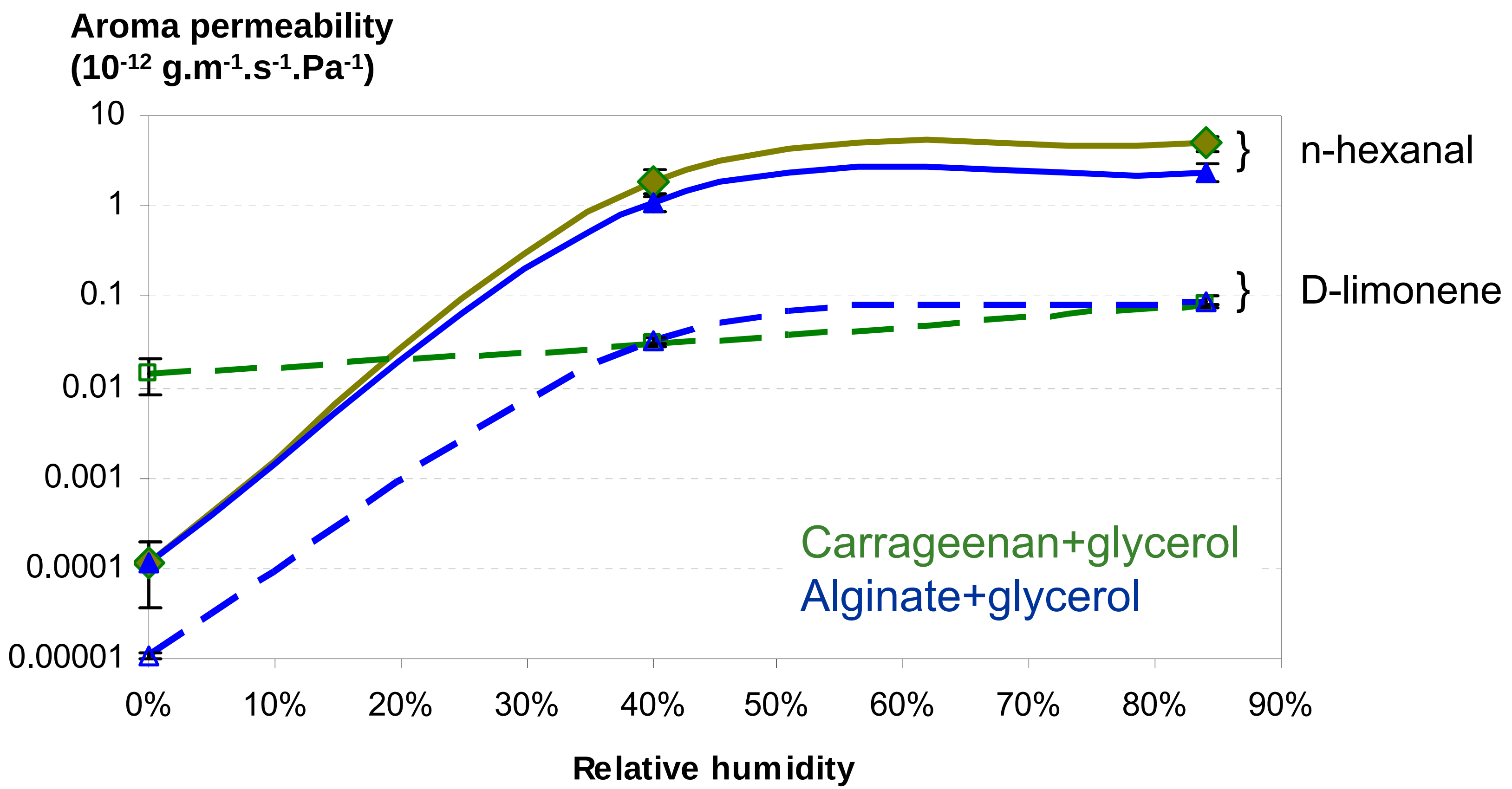


-CHOH of C6 of the methylcellulose interacts with the keton group of the 2-heptanone (displayed by FTIR-ATR) whereas the 2-pentanone favours the crystallization of methylcellulose (XRD)

Quezada-Gallo et al., J. Agric.Food Chem. 476 (1999) 108-113

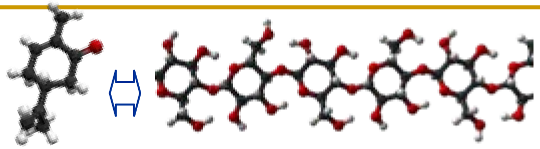


Not only the plasticizing effect of moisture can explain the aroma permeability through biopolymer networks

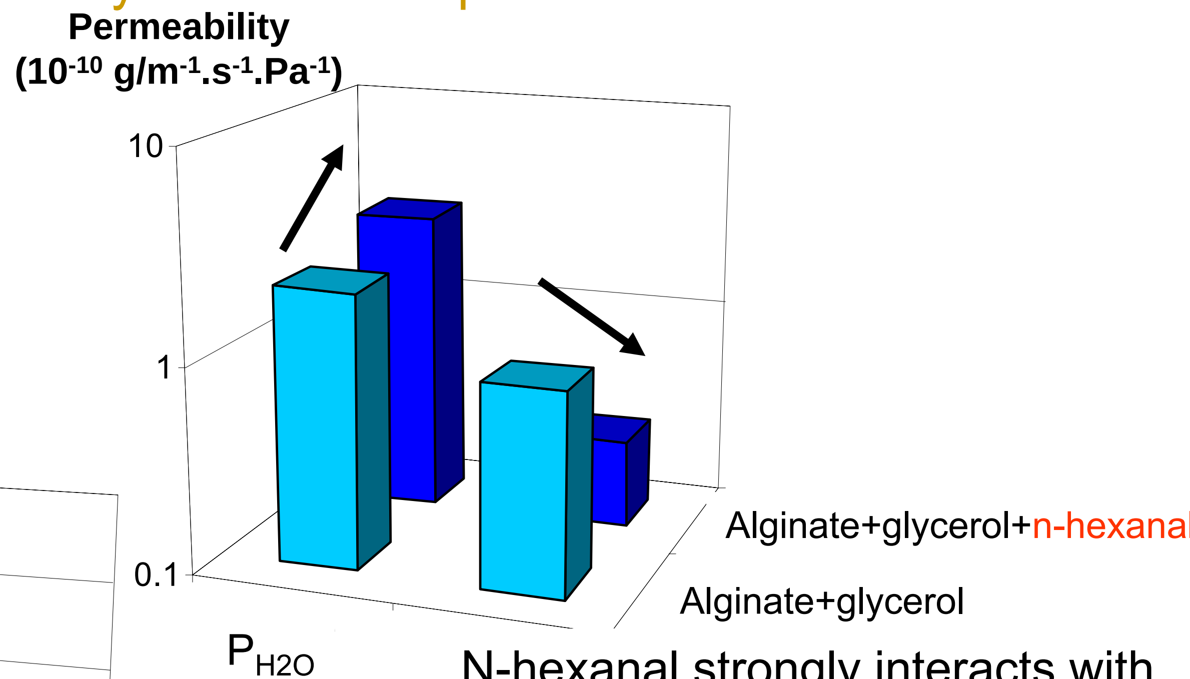


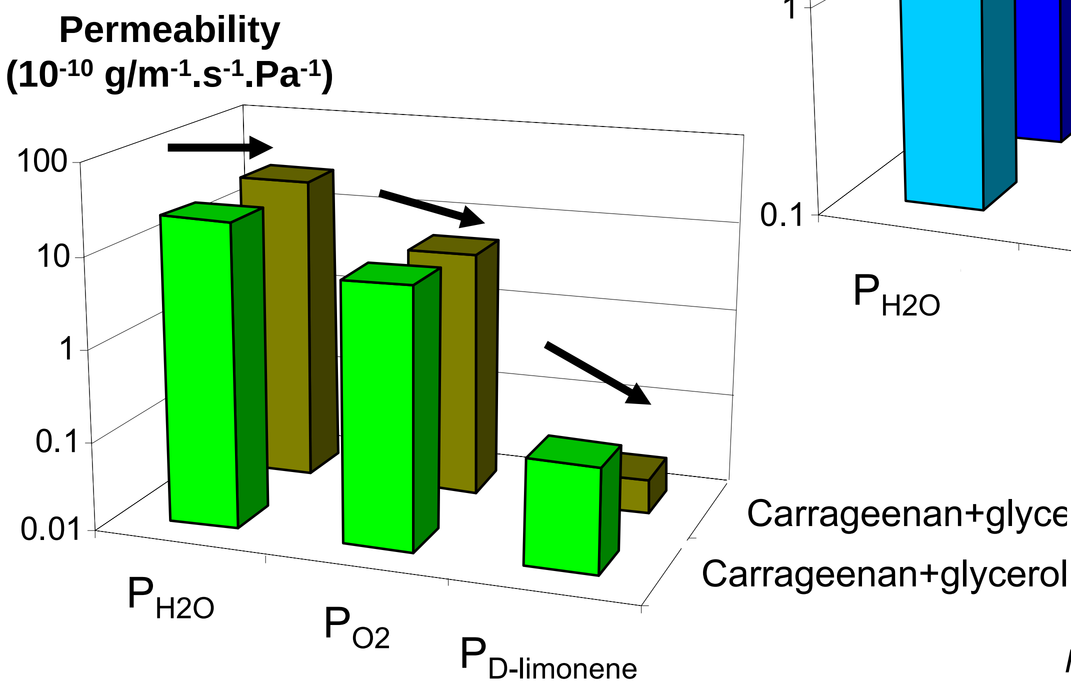
Hambleton et al. Biomacromol. 9(2008) 1058–1063
Hambleton J Food Eng 93 (2009) 80-88
Hambleton Food Hydrocolloids 23 (2009) 2116–2124

Diffusant – moisture – biopolymer interactions



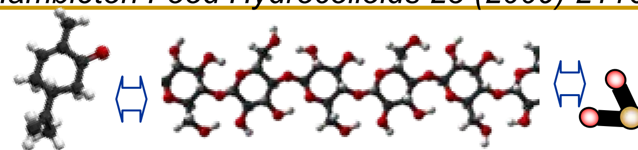
Aroma (n-hexanal) pre-encapsulated in biopolymer film modifies the structure that affects differently the diffusant permeabilities





N-hexanal strongly interacts with the OH of carrageenan to "crosslink" and then strengthens and increases film density (FTIR-ATR)
but in alginate ?????

Hambleton et al. Biomacromol. 9(2008) 1058–1063
Hambleton J Food Eng 93 (2009) 80-88
Hambleton Food Hydrocolloids 23 (2009) 2116–2124



Interaction between polymer and diffusant at the interface depends on the state of the diffusant : the Schroeder Paradox

For a same activity (same chemical potential) differential, the transfer rate through a dense membrane is often greater when the diffusing substance in contact to the membrane interface is at a liquid state.

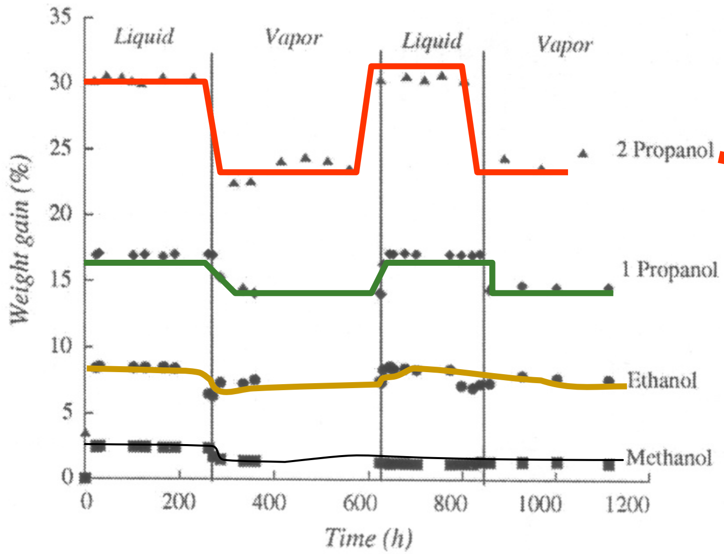


Fig. 2. Example of overall mass gain (M, expressed in percent) obtained with various compounds according to the protocol described in Fig. 1a with Silastic samples. Vertical lines indicate when the polymer sample has been transferred from one phase to the other. While the mass gain is the same for some compounds, significant, systematic and reversible differences are obtained for 1-propanol (♦) and 2-propanol (▲).

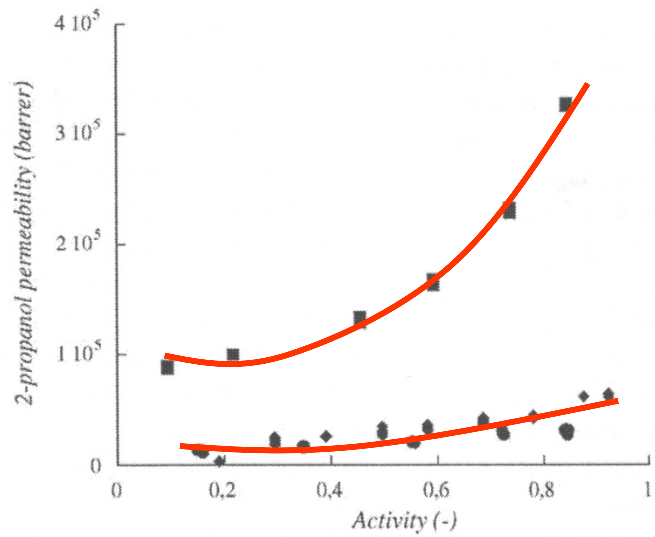
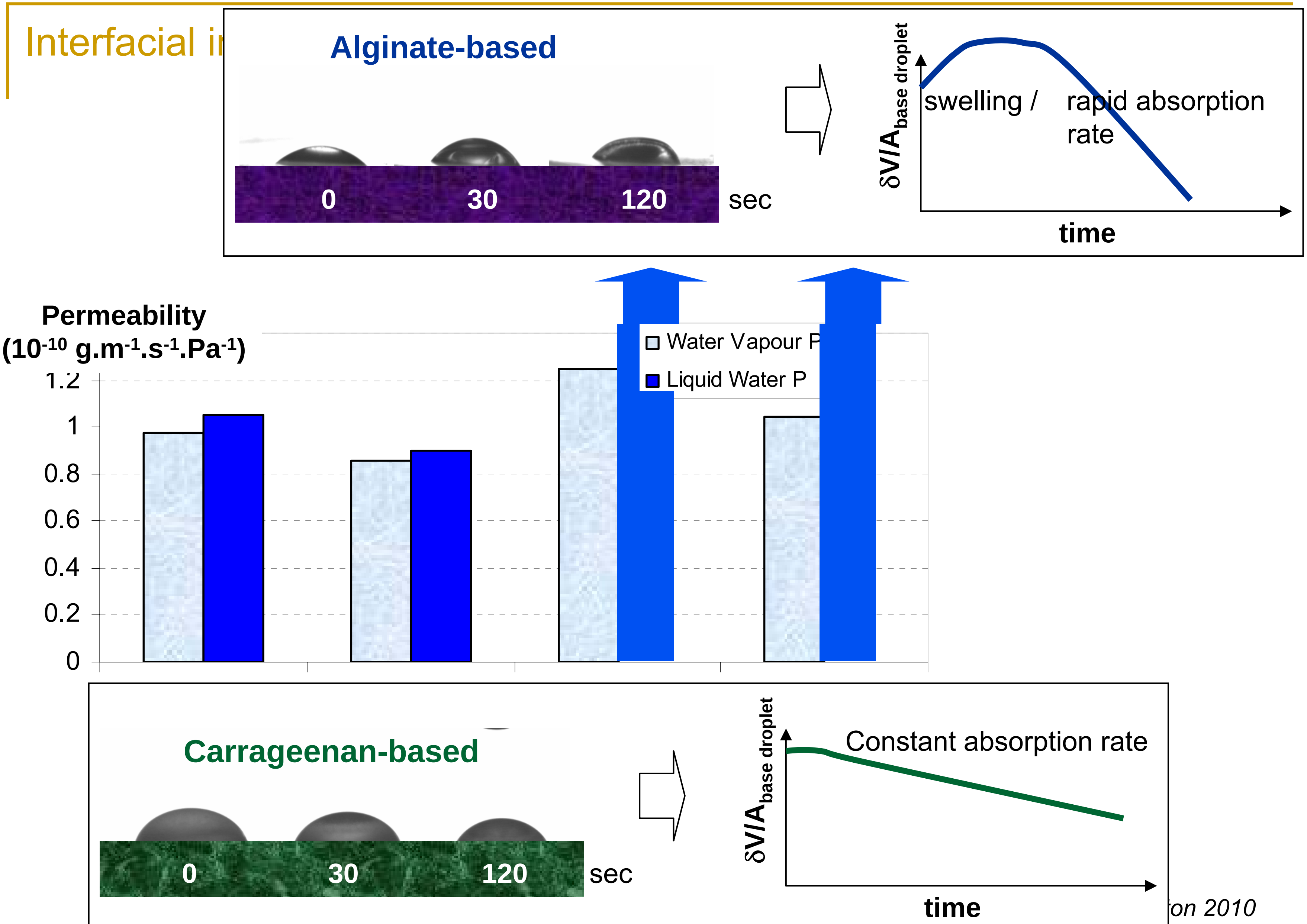


Fig. 7. 2-propanol permeability at 40 °C through a silicone rubber membrane (Silastic) obtained by different techniques: pervaporation, PV (■ pure liquid at the upstream side), vapor permeation, VP (♦ vapor at the upstream side, permanent regime), and time-lag, TL (● vapor at the upstream side, pseudo-steady regime).

Vallières et al. J. Memb. Sci., 278 (2006) 357–364

Interfacial i



on 2010

Interfacial interactions and state of diffusant

CONCLUSIONS

Interactions :

Water-water
Water-biopolymer
Water-plasticizer
Water diffusant-biopolymer
Interfacial / state of diffusant

affect

Functional properties of biopolymer based packaging (permeability, mechanical, …)

Needs to consider molecular or nanoscales phenomena in mass transfers mechanism through bio-polymer-based films and coatings

How to integrate physico-chemical parameter dealing with interactions in the shelf-life prediction models ?

Future challenge for scientists working on biopolymer-based packagings and coatings

Interactive conclusions

⇔

AKNOWLEDGEMENTS

Thanks to my PhD students

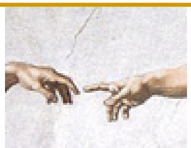
Alberto, Valérie, Claudine, Dong, Thomas, Eva, Alicia, Maria-José, Sabina… and their trainees

& to my colleagues from Dijon, Mexico, Udine, Valencia, and Warsaw

And a special thanks to Andrée Voilley who always interacts with me about thermodynamics and physico-chemical interactions occurring in mass transfers phenomena in edible films and coatings

Thank you for your attention

Scientist-teacher-student interactions



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