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Absorption of Water by Thin, Ionic Films of Gelatin

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This paper discusses absorption of water by thin, dry films of gelatin. Experiments using a wet-stamping technique were performed to characterize water uptake in terms of (i) equilibrium profiles of the water density inside the gel and (ii) the kinetics of water absorption. It was found that, in contrast to pure gelatin films, which absorb water approximately uniformly, films of gelatin doped with ionic additives have exponentially decaying equilibrium water profiles. The process of water absorption by both doped and undoped gels was described by a theoretical model based on the minimization of grand potential functional. The results of this model are in agreement with the experiment.

Introduction

The phenomena related to the osmotically driven swelling and shrinking of gels have attracted considerable scientific attention, largely because of their possible applications in transducing and sensory devices,^{1,2} microfluidics,³ photonics,⁴ separations science,⁵ and drug delivery.⁶ While most experimental^{7–9} and theoretical^{10–14} studies to understand the fundamental aspects of water uptake or release have focused on wet gels, the mechanism underlying the absorption of water by dry ones remains incompletely understood. Understanding permeation of water through dry gels would have implications for food^{15,16} and pharmaceutical industries,^{17,18} where dehydrated gel films are often used as protective coatings, and it is important to be able to predict and control the rates of their soaking/dissolution. Here, we study the absorption of water by thin (micrometers to tens of micrometers), dry films of either pure gelatin or gelatin doped with an inorganic salt (“ionic” films). We used a wet stamping (WETS) technique to controllably deliver water to both pure and the doped films of different thicknesses. From these experiments, we were able to deduce water profiles in the gels: these profiles were uniform in pure gels and exponentially decaying in the ionic ones. These observations are explained in the framework of a thermodynamic

model that describes transport of water into a gel as a diffusive process against a gradient of osmotic pressure.

Experimental Section

Figure 1a outlines the WETS procedure. Thin (1–80 μm) films of gelatin (Gelatin B, 225 bloom, Sigma-Aldrich) were prepared from a 10% (w/w) water solution of gelatin [pure or containing 1% (w/w) $\text{K}_4\text{Fe}(\text{CN})_6$] heated at 75 °C for 30 min and spin-coated onto flat glass surfaces. After gelation, the films were thoroughly dried for 48 h under vacuum and weighted on a precision balance, and their thicknesses were determined by profilometry. Water was delivered to the films from agarose stamps of dimensions 1 cm \times 1 cm \times 0.5 cm soaked in deionized water. The stamps were made from an 8% (w/w) solution of low-melting-point agarose (Omni Pur, EM Science, Darmstadt, Germany) in deionized water. This solution was microwaved for 2 min to dissolve the agarose, degassed for 1 min to get rid of bubbles, and poured into a flat-bottom glass container. After gelation (\sim 1 h at room temperature), the stamps were soaked in deionized water. Immediately prior to use, the surfaces of the stamps were dewetted by rolling on a tissue paper and by blowing dry nitrogen over them for \sim 15 s. A stamp was then placed onto and gently pressed against a surface of dry gelatin; once in conformal contact, water diffused from the stamp into the film. After a specified time, the stamp was removed, and water uptake by gelatin was quantified by weighing the wetted film.

To verify that agarose came into conformal contact with gelatin during stamping, stamps soaked in a 20% (w/w) solution of FeCl_3 were used. When iron ions diffused from these stamps into gelatin, they reacted with potassium hexacyanoferrate to give deep-colored Prussian blue; the intensity of the blue color was uniform throughout the stamped area. At the same time, the color of the stamps did not change (light orange), indicating that the flow of ions and water was always from the stamp into the dry gel and not in the opposite direction.

Stamping did not leave any residual water (e.g., by capillarity) on the surface of dry gelatin. When stamps were placed onto and immediately removed from the surface (contact times \sim 1 s), the mass of gelatin did not change. This was in sharp contradistinction to the situation when droplets of water were placed onto gelatin; even after immediate removal, they always left behind a layer of surface water.

Results and Discussion

Figure 1b shows a typical dependence of the amount of water $M(t)$ transferred from an agarose stamp into a film of dry gelatin [here, doped with $\text{K}_4\text{Fe}(\text{CN})_6$ and 32- μm thick] on the time of stamping t . The trends observed for this and other dry films fit to a $M(t) = M_{\text{eq}}[1 - \exp(-t/\tau_1)]$ function, where M_{eq} is a maximal (“equilibrium”) amount

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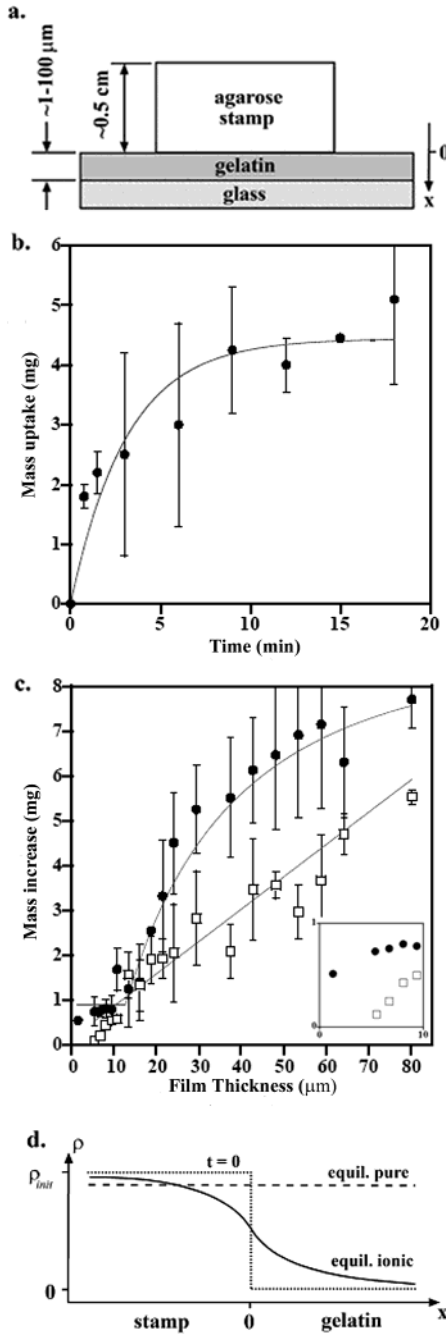


Figure 1. (a) Experimental setup used in WETS. (b) Typical time dependence of the amount of water transferred into an ionic gel from a stamp. Here, $L_g = 32 \mu m$ and $L_s = 0.5$ cm. The agarose stamp used had a surface area of 1 cm^2 . The curve fit is given by $M(t) = M_{eq}[1 - \exp(-t/\tau_1)]$, where τ_1 is ~ 6.5 min. (c) Equilibrium amounts of water transferred into gel films of different thicknesses. Identical agarose stamps were used in all stampings ($L_s = 0.5$ cm, surface area of 1 cm^2). Solid markers correspond to ionic gels [1% (w/w) of $K_4Fe(CN)_6$] and white markers to pure gels. The curve fit for ionic gels is defined by $M(L_g) = M_0$ if $L_g < L_0$ and $M(L_g) = M_0 + \beta\{1 - \exp[-(L_g - L_0)/\alpha]\}/\{2 - \exp[-(L_g - L_0)/\alpha]\}$ otherwise, and for pure gels, $M(L_g) = M_0$ if $L_g < L_0$, and $M(L_g) = M_0 + \beta(L_g - L_0)$ otherwise. The curves are least-squares regression fits to the data, with M_0 , L_0 , β , and α being fitting parameters. The thicknesses of the boundary layers, L_0 , estimated from these fits are $12 \mu m$ for ionic gels and $5 \mu m$ for pure ones. The inset is the blowup of the boundary layer region ($L_g < 10 \mu m$). (d) Qualitative equilibrium water profiles predicted by our theoretical model.

of water absorbed by a film and τ_1 is ~ 6.5 min. The equilibrium amounts of absorbed water depended on the thickness, L_g , of the gelatin film and on whether gelatin

was pure or ionic (i.e., doped with a salt; Figure 1c). For pure gelatin, the amount of absorbed water increased approximately linearly with L_g . For ionic gelatin, on the other hand, water uptake was characterized by a roughly sigmoidal curve: for very thin gels ($\sim 2 < L_g < \sim 10 \mu m$), M_{eq} was a slowly varying function of L_g (almost constant irrespective of the gel thickness), while for thicker ones it was well-approximated by an exponentially saturating dependence [i.e., a function of a $1 - \exp(-L_g)$ type].

In the following, we propose a theoretical model that (i) describes the adsorption of water by thin, dry gels and (ii) accounts for the observed differences between films of pure and ionic gels. This model also shows that our experimental results are not skewed by the stamping technique we used to deliver water to gelatin surfaces: it predicts water profiles in thin gels exposed to a reservoir (finite or infinite) of pure water to be the same as those obtained using the WETS technique (provided that the thickness of a stamp is much larger than that of a dry gel film).

The experimental system is modeled as two slabs made of porous, water-permeable materials. The first slab, representing a stamp, is uniformly soaked with pure water of initial concentration ρ_{init} ; the second slab is dry and contains a water-soluble salt. When the two stamps are brought into contact at time $t = 0$, water starts flowing from the stamp into the gel. Transport of water into the gel is driven by diffusion forces. In the process, water successively fills the pores and dissolves the salt contained in the gel. The solute molecules raise the pressure in the gel by Π (osmotic pressure), which can be approximated by the van't Hoff formula $\Pi = cRT$, where c is the molar solute concentration in the gel, R is the gas constant, and T is the absolute temperature. The excess pressure Π is assumed to be constant in the pores and is compensated by elastic forces exerted by the gel on the solution. It follows that the migration of water is linked with an increase in the elastic potential energy stored in the gel. The system reaches equilibrium when the diffusion is balanced by the gain in the elastic energy just discussed.

Water Profiles. Our goal is to determine two equilibrium profiles: (i) the profile of water in the gel, $\rho_g(x)$, and (ii) the “depleted” water profile in the stamp, $\rho_s(x)$. The actual water profile in the stamp is $\rho_{init} - \rho_s(x)$. In the following, $\rho_s(x)$ is referred to simply as the water profile in the stamp. Because the stamp is treated as the reservoir of water particles with a fixed chemical potential, the proper thermodynamic potential to be used for its description is the grand potential functional $\Omega = \Omega[\rho_g(x), \rho_s(x)] = U - TS - \Delta\mu\Delta M$, whose minimum corresponds to the equilibrium profiles of water in the stamp and in the gel. Here, U and S denote respectively the internal energy and the entropy of the system, $\Delta\mu$ is the difference in the chemical potential per unit mass of pure water in the stamp and the ionic solution in the gel, and $\Delta M = \int \rho_g(x) dx - \int \rho_s(x) dx$ is the amount of water transferred from the stamp into the gel. The internal energy of the system is given by $U = \gamma \int [\rho_g(x) + \rho_s(x)] x dx$ and represents the mechanical work needed to transfer an amount of water ΔM from the stamp into the gel¹⁹ with γ being a constant; the entropic term is given by $S = k_B \int [\rho_s(x) \ln \rho_s(x) + \rho_g(x) \ln \rho_g(x)] dx$ with k_B being the Boltzmann

(19) We neglect the contribution to internal energy originating from the change of the surface composition. The osmotic pressure is of the order of 10^6 N/m^2 ; the characteristic pressure corresponding to the surface tension is estimated as the ratio σ/α , where $\alpha \sim 50 \mu m$ is the characteristic penetration depth, and $\sigma \approx 7.0 \times 10^{-2} \text{ N/m}$ is the surface tension of water. Because $\sigma/\alpha \sim 10^4 \text{ N/m}^2$ is 2 orders of magnitude smaller than the osmotic pressure, this contribution due to the change of the surface composition can be neglected.

constant and represents the Gibbs–Shannon entropy of the distributions of water in the stamp and in the gel. In addition, the following constraints hold: $\int \rho_g(x) dx = \int \rho_s(x) dx$ for mass balance and $\rho_{\text{init}} - \rho_s(x=0) = \rho_g(x=0)$ for continuity. The equilibrium solution is found by minimizing the grand potential functional with respect to $\rho_s(x)$ and $\rho_g(x)$ and subject to the constraints specified previously. This procedure leads to the following system of equations:

$$\delta\Omega/\delta\rho_g(x) + \lambda_g = 0 \quad \text{and} \quad \delta\Omega/\delta\rho_s(x) + \lambda_s = 0 \quad (1)$$

where $\lambda_{g,s}$ are Lagrange multipliers and

$$\delta\Omega/\delta\rho_g(x) = -k_B T \ln[\rho_g(x)] - k_B T + x\gamma\Pi + \Delta\mu \quad (2)$$

$$\delta\Omega/\delta\rho_s(x) = -k_B T \ln[\rho_s(x)] - k_B T + x\gamma\Pi \quad (3)$$

Below, we briefly discuss solutions of eqs 1 for three different situations (Figure 1d):

(i) Stamp in Contact with Ionic Gelatin. The minimization procedure just described yields $\rho_{s,g}(x) = A_{s,g} \exp(-x/\alpha)$, where $\alpha = k_B T/\gamma\Pi$, $A_g = \rho_{\text{init}}[1 - \exp(-L_g/\alpha)]/[2 - \exp(-L_g/\alpha) - \exp(-L_s/\alpha)]$, and $A_s = \rho_{\text{init}} - A_g$. Parameter α can be treated as the water penetration/depletion depth at the stamp–gel interface. Because $\alpha \sim 50 \mu\text{m}$ (as calculated from the fit to the experimental data, see Figure 1c) is much smaller than the thickness of the stamp, $L_s \sim 0.5 \text{ cm}$, the normalizing constant A_g can be approximated by $\rho_{\text{init}}/[2 - \exp(-L_g/\alpha)]$.

(ii) Stamp in Contact with Pure Gelatin. In the case of pure gelatin (where $\Pi \approx 0$), the exponential solution derived in (i) can be approximated by linear functions. Water profiles are then uniform both in the stamp and in the gelatin: $\rho_{s,g}(x) = B_{s,g}$, with $B_g = \rho_{\text{init}}L_s/(L_s + L_g)$ and $B_s = B_gL_g/L_s$. Because $L_s \gg L_g$, one has $B_g \approx \rho_{\text{init}}$.

(iii) Infinite Reservoir of Water in Contact with Ionic Gelatin. In this case, the profile of water in the reservoir is constant, and that in the gelatin is the same as in (i).

Mass of the Absorbed Water. The amount of water $M(L_g)$ absorbed by a gelatin film of thickness L_g is related to the water profile in the film by the integral $M(L_g) = \int_0^{L_g} \rho_g(x) dx$. Using the equations for $\rho_g(x)$ derived in the previous section, our model predicts the following absorption characteristics:

(i) For ionic gelatin, the mass of absorbed water should vary with L_g as $M(L_g) = \rho_{\text{init}}[1 - \exp(-L_g/\alpha)]/[2 - \exp(-L_g/\alpha)]$. The experimental data agree with the predicted trend for $L_g \geq 12 \mu\text{m}$ (cf. Figure 1c). Below this value, absorption of water is almost constant irrespective of the gel thickness (Figure 1c, inset). We attribute this effect to the existence of a thin boundary layer whose physical properties are different from those of the bulk of the gel and for which our model does not account. Existence of such a layer was recently postulated on the basis of SPR experiments;^{20–22} we have observed that this layer shows anomalous, asymmetric water absorptivity²³ and its surface free energy²⁴ differs significantly from that of thicker gel films.

(ii) For pure gelatin, the amount of absorbed water should increase linearly with the gel's thickness, $M(L_g) = \rho_{\text{init}}L_g$. This prediction is in agreement with the experiment

(Figure 1c) above $L_g \geq 5 \mu\text{m}$. We note that the boundary layer for the pure gel appears to be thinner than that for the ionic one.

Kinetics of Water Absorption by Ionic Gels. The time evolution of the water profile $\rho(x)$ can be described by a Fokker–Planck equation²⁵ for diffusion against an external force:

$$\frac{\partial}{\partial t}\rho(x, t) = D\frac{\partial^2}{\partial x^2}\rho(x, t) + c\frac{\partial}{\partial x}\rho(x, t) \quad (4)$$

where D is the diffusivity of water. Because the equilibrium solution of eq 4 must correspond to the exponentially decaying water profile in ionic gels, $\rho_{s,g}(x) = A_{s,g} \exp(-x/\alpha)$, we find that $c = D/\alpha$. The solutions of eq 4 are found by expanding $\rho(x, t)$ into a power series $\sum_n a_n(t) \phi_n(x)$; functions $a_n(t)$ and $\phi_n(x)$ obey the following equations: $da_n(t)/dt = a_n(t)/\tau_n + D\phi_n''(x) + c\phi_n'(x) = \phi_n(x)/\tau_n$, where the prime denotes the spatial derivative and parameters τ_n are set by the boundary and initial conditions. It follows that $a_n(t) = C_n \exp(-t/\tau_n)$. The function $\phi_0(x)$ corresponding to the zeroth eigenvalue, τ_0^{-1} , is the equilibrium solution, $M_{\text{eq}} = M(t = \infty)$, of eq 4. The water uptake after time t is given by

$$M(t) = \sum_{n=0}^{\infty} C_n \exp(-t/\tau_n) \Theta_n$$

where $\Theta_n = \int_0^{L_g} \phi_n(x) dx$. In the limit of large t or if τ_1 is much larger than the rest of τ_n 's, all higher-order terms (i.e., $n > 1$) can be dropped, and the water content depends on time as $M(t) \approx M_{\text{eq}}[1 - \exp(-t/\tau_1)]$, in agreement with the experiment. The value of parameter τ_1 is evaluated from the least-squares fit to the experimental data to be $\sim 6.5 \text{ min}$. We note that the kinetics of water absorption for a pure gel ($c = 0$ in eq 4) is also approximated by an exponentially saturating function.

To conclude, water absorptivity of thin, dry gels depends on whether these gels are pure or doped with ionic additives. This result can have implications for engineering of thin coatings with controllable water-uptake characteristics. Because water profiles in ionic gels decay exponentially with depth, we expect such gels to be more resilient to wetting and to dissolve more slowly than pure gels exposed to water. Although the theoretical model we developed correctly predicts the wetting properties of the bulk of the gel films, it fails to account for the existence and properties of a thin layer close to the surface of the support. More work is needed to understand the origin, molecular structure, and properties of this layer.

(23) When a film of dry gelatin (ionic or pure) was peeled off from the glass surface and stamping was done on the film's backside (i.e., the side initially in contact with the glass support), the amounts of water transferred into the gel were significantly lower (by $\sim 50\%$) than for stamping on the top surface. Anisotropic absorptivity was also evidenced by the lack of blue color when stamps containing iron(III) chloride were applied to the back surface of the ionic gel containing potassium hexacyanoferrate. We also noted that the absorptivity of the backside slowly (\sim days) increased, although it never reached that of the top side. We hypothesize that this increase could be due to a slow structural rearrangement within the boundary layer after it had been separated from the glass support.

(24) Contact angles of water droplets on very thin films of dry gels were significantly higher than those of thicker gels (e.g., 60° on a $1.5\text{-}\mu\text{m}$ film vs 50° on a $32\text{-}\mu\text{m}$ one). At the same time, water droplets spread more rapidly on thin gels than on thicker ones. For example, after 15 min, the contact angle on a $1.5\text{-}\mu\text{m}$ film was 18° , while that on a $32\text{-}\mu\text{m}$ film was 35° .

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