Kinetics of the Osmotic Hydration of Chickpeas

Gabriel Pinto*

Departamento de Ingeniería Química Industrial y del Medio Ambiente, E.T.S.I. Industriales, Universidad Politécnica de Madrid, 28006 Madrid, Spain; **gpinto@iqi.etsii.upm.es*

Ali Esin

Department of Food Engineering, Middle East Technical University, Ankara 06531, Turkey

It is widely accepted that presenting real-life examples and activities in the classroom increases students' enthusiasm to learn and understand the principles in chemistry *(1–3)* and science *(4–7)* in general. This article is a continuation of a program intended to help chemistry instructors make connections between students' everyday experiences and chemical principles taught in the classroom *(8–14).* A straightforward experience introducing students to several concepts, found in university-level freshmen and sophomore chemistry, physics, calculus, and biology classes, allows the quantitative explanation of a process familiar to students: the swelling of chickpeas in water.

Chickpea (*Cicer arietinum*) is a widely-used plant of the leguminous family. Most students know that chickpeas (and other legumes or fruits, such as dried plums) swell in water. As water enters the chickpea, the concentrated solution within the chickpea is diluted. Conversely, a cucumber shrinks into a pickle in brine because water leaves the comparatively dilute solution within the cucumber. The study of water absorption by dried legumes is pertinent because this is a step in their industrial preparation *(15, 16)* and could serve as an example to make students aware of questions arising in the food industry.

As noted by Konak *(17),* skins around fruit and vegetables act as osmotic membranes. An adequate explanation of osmosis can be found in most chemistry textbooks *(18),* where important and varied practical applications of this phenomenon, such as desalination of saltwater by reverse osmosis, are cited. Unfortunately, in chemistry courses osmosis is usually reduced to the calculation of the osmotic pressure of hypothetical solutions. A simple demonstration model of osmosis was discussed by Morse *(19)* in this *Journal.*

In a general chemistry course, this experiment could serve as an introduction to the concepts of osmosis, mass transfer, and diffusion. The simplicity of the procedure lies in the fact that only mass measurements are taken over time, so hydration is directly observed and monitored. In this experiment students measure the rate at which water is absorbed by dried chickpeas. Measurements are made at several temperatures, using water and salt solutions. By calculating the initial hydration rate at different temperatures, an Arrhenius-type activation energy can be estimated.

The proposed experiment is inherently safe and inexpensive to do. It can be done in the laboratory or, at least partially, as a take-home project in a kitchen, given the fact that the materials needed, such as a balance, are easy to obtain or frequently found at home. Although an analytical balance was used in the laboratory, students performing the experiment at home would not need a balance that weighs to as many decimal points. Another possibility for this experiment is to perform it with a biology or physics instructor, as an interdisciplinary activity. Measurement, graphing of data, and modeling are all combined in this experience.

Theory

Mass transfer is the molecular scale movement of a substance through a medium under a concentration gradient in the direction of decreasing concentration. The rate of the transfer depends on the degree of departure of the system from equilibrium and ends when equilibrium is attained. For example, when a wet piece of cloth is placed in a stream of air, at the surface of the cloth, molecules of water vaporize and diffuse through into the main portion of the air stream, where they are carried away and the cloth dries. The process ends when equilibrium is attained between the concentration of water vapor in the air and the concentration of water vapor at the surface of the cloth.

Diffusion is the net movement of molecules from a region of greater concentration to a region of lesser concentration in search of equilibrium. Across a membrane, water moves in two directions, not only one direction. At equilibrium, the net result is a decrease of concentration in the more concentrated region and an increase in the concentration of the less concentrated region. We call this process osmosis when diffusion takes place across a membrane. Thus osmosis is the movement of water across a semipermeable membrane from an area of higher concentration of water to an area of lower concentration of water. Owing to the complex morphology of plant tissues, mass transfer in osmotic hydration or rehydration of cellular plant foods, such as fruits and vegetables, involves several physical effects of transport mechanism, such as osmosis, diffusion, hydrodynamic mechanism penetration, and others *(20).*

Under isothermal conditions, the kinetics of moisture absorption by foods, such as cereal grains or legumes, can be modeled by the Peleg equation. Peleg *(21)* first introduced the model to describe moisture absorption by milk powder and rice. This model may be represented by the following equation,

$$M(t) = M_0 + \frac{t}{k_1 + k_2 t} \qquad (1)$$

where $M(t)$ and M_0 are the moisture content of the solid (w/w) at times $t > 0$ and $t = 0$, respectively, and k_1 and k_2 are rate constants. According to this model, the equilibrium moisture, M_E, is asymptotically attained; that is, when $t \rightarrow \infty$:

$$M_E = M_0 + \frac{1}{k_2} \qquad (2)$$

Similarly, the instantaneous absorption rate, $dM(t)/dt$, is given by,

$$\frac{dM(t)}{dt} = \frac{k_1}{(k_1 + k_2 t)^2} \tag{3}$$

and the initial rate, that is, the rate at $t = 0$, is given by $1/k_1$. A general feature of mathematical relations such as eq 1 is that they can be transformed to a linear relationship in the form:

$$\frac{t}{M(t) - M_0} = k_1 + k_2 t \tag{4}$$

In this experiment, as a result of the negligible initial equilibrium moisture content of the chickpeas at room conditions, we assume $M_0 = 0$ and eqs 1–4 may be simplified.

This model, as pointed out by Peleg *(21),* is an empirical model that was not derived from any set of physical laws or diffusion theories. But in our case, if experimental data fit acceptably with it, the equation is very useful for the calculation of initial absorption rate, in accordance to eq 3. Some important relations mathematically analogous to the Peleg equation are the Langmuir-type absorption isotherm and the Michaelis–Menten kinetic expressions. Water absorption has also been described in the literature by models assuming that the process is controlled by mass transfer or by assuming that the water diffusion inside the food is the rate-controlling step.

Experimental Procedure

Chickpeas were purchased at a local market in León, Spain; however, other legumes would be adequate. In fact, the described experiment could be used to compare the absorption patterns of different chickpeas cultivations and other legumes such as beans or lentils.

A sample of 20 chickpeas was studied in each experimental series. Chickpeas were selected in terms of weight (~0.7 g), size (10.6 ± 0.2 mm of diameter), and aspect (homogeneity). Samples selected for each run were weighed on an electronic balance (± 0.0001 g) and immersed in a beaker containing 200 mL of distilled water or aqueous solutions of NaCl up to 3.0 M, at 20 ± 1 °C (room temperature). At selected intervals, samples were quickly removed with a spoon, gently wiped with clean paper towel, and weighed. Clean towels must be used for each weighing to avoid contamination with salt or water. The moisture uptake (MU) was calculated as follows,

$$\text{MU}(t) \equiv \frac{(\text{mass CP})_t - (\text{mass CP})_0}{(\text{mass CP})_0} \tag{5}$$

where CP stands for chickpeas.

The experiment was repeated with new samples of chickpeas at temperatures of 5, 30, 40, and 50 °C. For these temperatures, the beaker was immersed in a thermostatic bath set at the predefined constant temperatures. The precision on temperature measurements was ± 1 °C.

There are not data for times longer than 270 min (4.5 hours). At longer times the chickpeas became biologically, chemically, and physically unstable at temperatures of 40 and 50 °C, as a result of fermentation, as showed by the formation of foam.

Figure 1. Appearance of five chickpeas after different times of soaking in distilled water at 20 °C. Coins of one dime (United States), 2 cents (European Union), and 10 kopecs (Russia) were included for comparison.

Hazards

There are no significant hazards associated with this experiment. Nevertheless the students should be advised not to eat fermented chickpeas (after a long soaking in hot water).

Results and Discussion

The swelling of chickpeas when soaked in water is illustrated in Figure 1. In accordance with experimental weight data, the adsorbed water at the surface of the chickpea that cannot be wiped off is negligible in comparison with the absorbed water, being less than 0.5% of the chickpea's weight in each case. The repetition of the experiment showed a good reproducibility of measurements. Typical results in the variation of the mass of chickpeas during soaking as a function of time show characteristic asymptotic curves, as observed in Figures 2 and 3. Figure 2 illustrates the variation of moisture

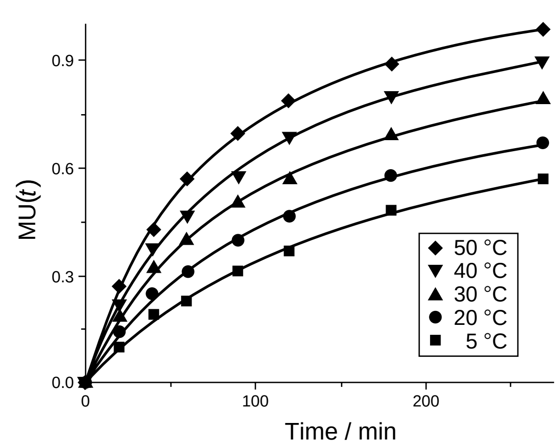

Figure 2. Graph of the moisture uptake for chickpeas immersed in distilled water at different temperatures.

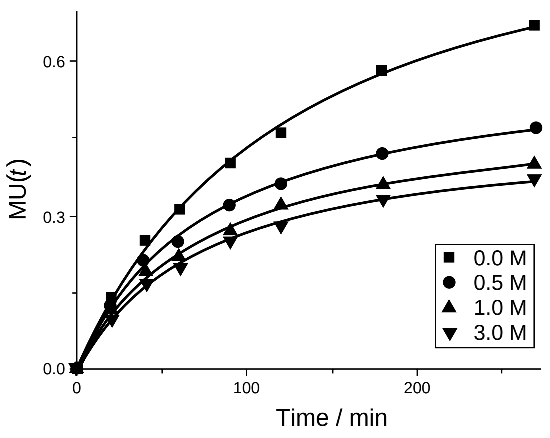

Figure 3. Graph of the moisture uptake for chickpeas immersed in differing concentrations of aqueous solutions of NaCl; T = 20 °C.

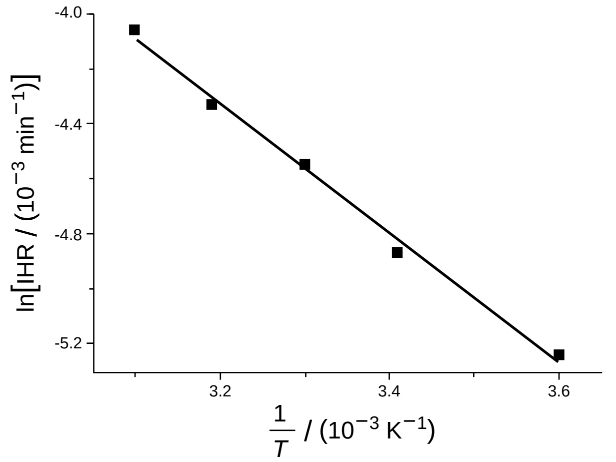

Figure 4. Graph of natural logarithm of the initial hydration rate (IHR) as a function of reciprocal temperature.

uptake with the immersion time during osmotic hydration over a range of temperatures. Figure 3 shows the variation of moisture uptake with immersion time with varying NaCl concentrations of the immersion solution.

The values of the parameters of the Peleg model, the equilibrium moisture uptake (M_E), taken as $1/k_2$, and the initial rate of hydration, taken as $1/k_1$, for the different samples are listed in Table 1. As expected, the hydration rate increases with temperature, owing primarily to the combined effect of increasing diffusivity and decreasing viscosity. According to an Arrhenius-type behavior the semilog plot in Figure 4 predicts the temperature dependence of the initial hydration rate (IHR) as,

$$\text{IHR} \equiv \left(\frac{\text{d MU}(t)}{\text{d}t}\right)_0 = \left(24.8 \pm 7.0 \text{ min}^{-1}\right)\exp\left[\frac{(-2.35 \pm 0.11)10^3\text{ K}}{T\text{ K}}\right] \quad (6)$$

where T is the absolute temperature. The correlation coefficient of −0.9970 is obtained.

From the slope of this plot, $-E_a/R$, the apparent energy of activation, E_a, was calculated as 19.5 ± 0.9 kJ/mol. This value agrees well with the literature value of 17 kJ/mol for the activation energy of fluidity of water *(22),* which measures the temperature dependence of the viscosity of water. The fluidity of water is relevant to its molecular mobility in pores and slits, such as in the process studied in this experiment. As pointed out by several authors *(23, 24),* when a rate is controlled by chemical reaction and thus related to classical collision theory, the E_a is generally higher than that expected for a diffusion-controlled process, which generally exhibits E_a of only a few kilojoules per mole. Thus, as expected, the studied process appears to be a diffusion-controlled process and E_a is associated with the energy barriers, such as softening of the cell walls, that must be overcome for water to flow and diffuse into the chickpeas. This result gives insight into the mechanism of the process. Generally the mass transfer coefficient increases with temperature.

Table 1. Water Absorption Parameters, Equilibrium Moistures Uptake, M_E, and Initial Hydration Rates Calculated from Experimental Data

T/°C	[NaCl]/(mol L^{-1})	k_1/min	k_2	M_E	Initial Hydration Rate/(10^{-3} min^{-1})
5	0.0	190 ± 7	1.05 ± 0.05	0.95 ± 0.05	5.3 ± 0.2
20	0.0	130 ± 5	1.02 ± 0.03	0.98 ± 0.03	7.7 ± 0.3
30	0.0	94 ± 3	0.93 ± 0.02	1.08 ± 0.02	10.6 ± 0.3
40	0.0	76 ± 2	0.83 ± 0.02	1.20 ± 0.03	13.2 ± 0.3
50	0.0	58 ± 1	0.79 ± 0.01	1.27 ± 0.02	17.2 ± 0.3
20	0.5	131 ± 4	1.66 ± 0.04	0.60 ± 0.02	7.6 ± 0.2
20	1.0	145 ± 6	1.97 ± 0.05	0.51 ± 0.01	6.9 ± 0.3
20	3.0	164 ± 6	2.13 ± 0.05	0.47 ± 0.01	6.1 ± 0.2

Further Discussion: Uniqueness of a Model

The Arrhenius equation was originally developed for simple chemical reactions where the energy of activation has a precise meaning. From the reported data it can be deduced that the logarithm of the initial hydration rate, IHR, when plotted versus the absolute temperature reciprocal, yields a straight line in the temperature range considered. But the reported experimental data can be fitted by a variety of alternative mathematical models, for example,

$$\ln(\mathrm{IHR}) = -12.55 + 0.0263T \qquad (7)$$

with a correlation coefficient of 0.9999, or

$$\mathrm{IHR} = 5.0 \times 10^{-3} + 2.27 \times 10^{-5}(T - 273)^{1.61} \qquad (8)$$

with a correlation coefficient of 0.9999. A discussion of a model's uniqueness and the need to establish the meaning of experimental parameters by independent assays will be of great educational value to the students. The variation of initial hydration rate with the NaCl concentration in the immersion solutions is shown in Figure 5. Results are in accordance with the expectation that the increased salt concentration in the immersion liquid results in the decrease of hydration kinetics. The process of diffusion, which students know from physics, can be used as a platform to introduce the concept of mass transfer and also the basic equation for transfer processes:

$$\text{Transfer rate per unit area} = \frac{\text{driving force}}{\text{resistance}} \qquad (9)$$

In our case, according to eq 9, which is only a first-order law, the initial moisture uptake rate $(\mathrm{d}M(t)/\mathrm{d}t)_0$ can be described by the expression,

$$\left(\frac{\mathrm{d}M(t)}{\mathrm{d}t}\right)_0 = SK_{\mathrm{tr}}\,\Delta C \qquad (10)$$

where S is the surface area for mass transfer, K_{tr} denotes the mass transfer coefficient, and ΔC is the difference between concentration of salts in the chickpeas and in the immersion liquid. The work by Machado et al. *(25)* is recommended for further reading on different mathematical models to describe the kinetics of moisture uptake of foods during soaking processes.

It should be stressed that a successful curve fitting is not a confirmation of a hypothesis. The true test is to use the model to estimate the moisture gain after 6, 12, or 24 hours of immersion and then compare the estimates with the values actually recorded.

Further Studies

It would be interesting to complement the absorption data by size (radius) and hardness measurements and microscopic analysis in order to follow the structural changes occurring in the chickpeas, or with other assays that could monitor the structural changes in the starch and protein molecules, given the fact that transitions from a glassy solid state to the rubbery liquid state is also appreciated in the process *(26)*. This experiment could also be performed for other legumes such as lentils or beans and with other salt solutions such as $NaHCO_3$. It is known that with dried vegetables, especially beans, peas, and chickpeas, a pinch of sodium bicarbonate added to the soaking water improves the cooking abilities of these legumes. Use of soft water, preferably distilled, for soaking is also recommended as calcium and magnesium ions increase the firmness.

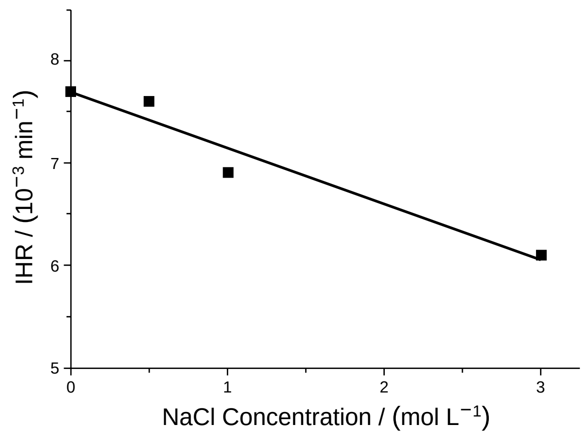

Figure. 5. Graph of the natural logarithm of the initial hydration rate (IHR) as a function of NaCl concentration of the immersion solution.

Summary

This simple kinetics experience assists in teaching the concepts of osmotic flow, mass transfer, diffusion, kinetics of hydration, modeling, and estimation of activation energy. The experiment can be safely, inexpensively, and easily performed. It will enable the students to generate and interpret quantitative experimental data while investigating a familiar physical phenomenon with practical implications. The experiment performs the role of introducing first-year students to an interdisciplinary phenomenon.

In a broader sense, this experiment could be used to introduce students to the importance of the water cellular flow in living organisms. The importance of this area was acknowledged with the award of the 2003 Nobel Prize in Chemistry to Peter Agre and Roderick MacKinnon, who have made fundamental discoveries of how water and ions move through membranes *(27)*. Agre discovered and characterized the first water channel protein and MacKinnon elucidated the structural and mechanistic basis for ion channel functions. Water channels are crucial for life and are found in all organisms from bacteria to humans *(28)*. In plants, they are critical for water absorption in the root and for maintaining the water balance through the plant.

Acknowledgments

The authors would like to gratefully recognize the financial support provided by the *Fundación Española para la Ciencia y la Tecnología* (Spanish Foundation for Science and Technology) under the project “Teaching/Learning of Chemistry and Everyday Life” (Grant No. 17502/57-1F). We would also like to thank the reviewers and editors for useful and thought-provoking suggestions.

Literature Cited

1. Roesky, H. W.; Möckel, K. *Chemistry Curiosities;* VCH: Weinheim, Germany, 1996.
2. Jones, M. B.; Miller, C. R. *J. Chem. Educ.* **2001,** *78,* 484.
3. Beauchamp, G. *J. Chem. Educ.* **2001,** *78,* 523.
4. *Essays in Physical Chemistry;* Lippincott, W. T., Ed.; American Chemical Society: Washington, DC, 1988.
5. Van Wie, B. J.; Poshusta, J. C.; Greenlee, R. D.; Brereton, R. A. *Chem. Eng. Educ.* **1994,** *28,* 188.
6. Steidle, C.; Myers, K. J. *Chem. Eng. Educ*. **1999,** *33,* 46.
7. Fraser, D. M. *Chem. Eng. Educ.* **1999,** *33,* 190.
8. Zubizarreta, J. I.; Pinto, G. *Chem. Eng. Educ.* **1995,** *29,* 96.
9. Pinto, G. *J. Chem. Educ.* **1998,** *75,* 725.
10. Pinto, G. *Educ. Chem.* **2000,** *37,* 71.
11. Pinto, G. *Educ. Chem.* **2001,** *38,* 150.
12. Pinto, G. *Anales de la Real Sociedad Española de Química* **2003,** *99* (1), 44.
13. Pinto, G.; Rohrig, B. *J. Chem. Educ.* **2003,** *80,* 41.
14. Pinto, G. *Educ. Chem.* **2003,** *40,* 11.
15. Singh, U. *Qual. Plant Foods Human Nutr.* **1985,** *35,* 339.
16. Afacan, N. Determination of the Important Parameters for High Quality White Roasted-Chickpea Production. M.Sc. Thesis, Middle East Technical University of Ankara, Turkey, 2000.
17. Konak, A. R. *Chem. Eng. Educ.* **1997,** *31,* 40.
18. For an example, see Fine, L. W.; Beall, H.; Stuehr, J. *Chemistry for Scientists and Engineers,* Preliminary Ed.; Saunders College Publishing: Philadelphia, PA, 2000.
19. Morse, J. G. *J. Chem. Educ.* **1999,** *76,* 64.
20. Barat, J. M. E.; Chiralt, A.; Fito, P. *J. Food Sci.* **1998,** *63,* 836.
21. Peleg, M. *J. Food Sci.* **1988,** *53,* 1216.
22. Metz, C. R. *Shaum's Outline Series, Theory and Practice of Physical Chemistry;* McGraw-Hill: New York, 1976.
23. Rydberg, J.; Musikas, C.; Choppin, G. R. *Principles and Practices of Solvent Extraction;* Marcel Dekker: New York, 1992.
24. Paz, I.; Pinto, G. *Spectrosc. Letters* **2002,** *35,* 357.
25. Machado, M. F.; Oliveira, F. A. R.; Gekas, V.; Singh, R. P. *Int. J. Food Tech.* **1998,** *33,* 225.
26. Blanshard, J. M. V.; Lillford, P. J. *The Glassy State in Foods;* Nottingham University Press: Loughborough, United Kingdom, 1993.
27. Nobel e-Museum: Nobel Prize in Chemistry 2003. *http://www.nobel.se/chemistry/laureates/2003* (accessed Feb 2003).
28. Agre, P.; King, L. S.; Yasui, M.; Guggino, W. B.; Ottersen, O. P.; Fujiyoshi, Y.; Engel, A.; Nielsen, S. *J. Physiol.* **2002,** *542,* 3.