

Water Activity and Food

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Foreword

It is not yet 200 years since Cavendish (1781) discovered that water was a compound produced when hydrogen was burned in oxygen. It is also less than 100 years since van't Hoff (1887) announced the relationship between osmotic pressure and the molecular weight of solutes. In the same year (1887-1888) Raoult showed that the molecular weight of solutes could also be determined by measuring the vapor pressure of solutions. Against these landmarks in the progress of science, we can note that it is only during the last 20 years that the use of water activity to describe the water status of the environment has gained increased acceptance by microbiologists and, more recently, by food scientists and technologists. And now we have a book, "Water Activity and Food," by two authors who are both very well qualified to write on water activity as a factor in the water relations of microorganisms, and in food processing and storage.

After an introductory chapter on water in foods and in solutions, and a second chapter on methods, there follow two chapters dealing with the water relations of enzyme activity, lipid oxidation, nonenzymatic browning, and several other food-related factors. The water relations of microbial growth, the effects of water on microbial survival, the spoilage and preservation of foods at various levels of water activity, and the water relations of food-borne pathogens are next discussed in some detail. The final three chapters deal with the importance of water activity in nonmicrobiological aspects of food processing and storage. Throughout the book, the authors examine the literature from an " a_w point of view," and give numerous examples of the value of water activity as a basis for predicting the reactions of microorganisms or the stability of food components. They also report on some examples where water activity has been a somewhat inadequate predictor of events, and on a number of interesting interactions with other environmental parameters.

No matter how useful the concept of water activity may be in certain applications in food science and technology, it should not be expected to explain everything. Water activity is, after all, simply a number which provides information about the vapor pressure of water in a system. While it describes the exact percentage of water molecules in a system which has the characteristics of pure water, it tells us nothing of the nature of the forces binding the remainder. It is, in

fact, nothing more than a statement of the average properties of all the water molecules in the system. A proper understanding of the role of water in complex systems, such as living cells and foods, must depend on much more detailed information about all the properties of the water molecule and its constituent ions, and of their interactions with the great variety of molecules and ions in the environment. The task is undoubtedly formidable but the steadily increasing array of physical methods for the study of such interactions will enable some progress to be made.

Addressed as it is to food scientists and technologists, this book should help to bring a more enlightened approach to studies of foods and their associated microorganisms, in relation to the water status of the environment. It should assist food technologists interested in developing new products and processes to make the best use of present knowledge about the significance of water in foods. It should also stimulate other investigators to measure and control water activity in experiments in which the role of water is being studied. In this way, we shall be able to fill in some of the obvious gaps in our knowledge and will soon discover whether a_w can be replaced by something more meaningful or whether, like pH, it will be something to measure and consider for perhaps another 100 years or so.

W. J. SCOTT

Preface

Throughout the past twenty-five years, the importance of water activity in foods has received emphasis in the work of food microbiologists. Over a similar period, chemists have likewise paid attention to its influence in enzymatic and non-enzymatic reactions in foods. Physicists, too, have long considered the effects of relative humidity, water activity, and other manifestations of water vapor pressure, particularly as these relate to matters of heat and mass transfer in foods. Indeed, in all of these disciplines, there exist specialized reviews of water activity and its significance in foods.

However, it is the authors' impression that only relatively recently—since the discussions on intermediate moisture foods—has the food technologist become fully aware of the importance of water activity in both food preservation and processing. Our intention, therefore, is to give the food technologist an overview of the influence of water activity on the systems with which he is concerned. Accordingly, we have omitted both detailed considerations of the theory of water structure, and in-depth discussions of the physiological basis of microbial water relations. It is our hope that this book, while being of assistance to food technologists, may permit those in specialist disciplines to appreciate the significance of water activity in areas of food science outside their own fields.

The book is organized to proceed from the particular to the general, that is, from physical and chemical aspects to microbiology, food processing and storage, and sanitation. At the risk of some overlap, we have included a section on pathogenic microorganisms separate from that dealing with general microbiological considerations. It is felt that many readers will appreciate this special treatment.

In attempting a broad coverage of this topic, we have relied heavily on the advice of colleagues. Scientists of both the CSIRO Division of Food Research and The Procter & Gamble Company Winton Hill Technical Center have been most helpful with comment and criticism. We also are especially indebted to A. C. Baird-Parker, T. P. Labuza, W. J. Scott, and J. G. Voss, all of whom contributed invaluable suggestions and advice. However, the responsibility for the text rests solely with the authors who conceived and wrote it. Finally, we acknowledge, with thanks, our wives, Betty and Jacky, who, although a hemisphere apart,

shared many of the concerns and frustrations attendant to the genesis of this volume.

JOHN A. TROLLER
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1

Water Activity—Basic Concepts

WATER IN FOODS

All foods contain water, and it is a common observation that the foods most likely to show rapid deterioration due to biological and chemical changes are usually those of high water content. The application of this principle precedes recorded history, but at some stage, our early ancestors found that spoilage could be delayed or prevented by using the available means to dry perishable foods, particularly the flesh of beast, fish, and fowl. The heat of fires, the sun's radiation, and even the sublimation of ice at high altitudes or high latitudes produced items of diet that could be kept for later consumption without many of the adverse changes apparent when the untreated material was so stored. Smoking, presumably an accidental adjunct to the drying of flesh over fires, added antimicrobial substances that augmented the stabilizing effect of drying.

The water in foods serves as solvent for many constituents, and any drying process will concentrate these solutions. If it is increasing concentration, rather than decreasing water content per se, that preserves food, other methods of increasing the concentration of a food's aqueous phase should also enhance its stability. Such alternatives as salting and syrupeing do preserve foods by increasing solute concentrations. The salting of pork for shipboard use in the days of sail is a classic example. Historically, the combination of salting and drying was used commonly for foods of animal origin, and, later, syrupeing and drying were utilized for the preservation of fruits.

Thus, the study of water in foods is in large part a study of aqueous solutions in which the solutes, by dint of both their nature and concentration, alter the physical properties of the solvent. Removing water from foods and adding solutes to foods have demonstrably similar, but rarely identical effects upon, for

example, their resistance to microbial attack. When the food solution has been concentrated to the point at which microbial growth is controlled, susceptibility to certain undesirable chemical and physical changes becomes apparent. Greater increases in concentration may be required to control these enzymatic and nonenzymatic changes which influence, in particular, the taste and appearance of food.

The water-related criteria that have been used in studies of the stability of foods include water content, solute concentration, osmotic pressure, equilibrium relative humidity (E R H.), and water activity (a_w). Water content and solute concentration tell little about the properties of the water present in the food. However, the other indices are measurements of related colligative or osmotic properties and appear to be good indicators of the availability of the water to participate in reactions. All are not equally appropriate to food—the use of osmotic pressure presupposes the presence of a membrane of suitable permeability, and equilibrium relative humidity refers strictly to the atmosphere in equilibrium with a food, not to the food itself.

This book is concerned with the remaining parameter, a_w . There is now wide agreement that a_w is the most useful expression of the water requirements for, or water relations of, microbial growth (Scott, 1957) and enzyme activity (Acker, 1962). The alternatives of solute concentration and water content have been shown very clearly by Scott (1962) to be inadequate for describing the availability of water for the multiplication of certain bacteria (see Chapter 5, Table 5.2).

The expressions referred to above all relate to equilibrium conditions. However, in many situations of concern in food technology, the water in a food is not in equilibrium with the water vapor in its surroundings. In such cases, the water content of the food will change with time, and this may have profound effects on the stability of the food. These considerations are particularly relevant to the packaging and storage of foods and will be discussed in later chapters.

PROPERTIES OF SOLUTIONS

When solutes are dissolved in water, entropy is decreased as water molecules become oriented with respect to solute molecules. Water molecules are less free to escape from the liquid into the vapor phase, and the vapor pressure is lowered. Consequent upon this are the depression of freezing point and the elevation of boiling point. The relationship between concentration and vapor pressure for ideal solutions is given by Raoult's law. This law states that for ideal solutes, the relative lowering of the vapor pressure of the solvent is equal to the mole fraction of the solute.

If p and p_0 are the vapor pressures of solution and solvent, respectively, and if

n_1 and n_2 are the number of moles of solute and solvent, respectively, Raoult's law may be expressed

$$\frac{p_o - p}{p_o} = \frac{n_1}{n_1 + n_2} \quad (1)$$

As 1 kg of water contains 55.51 moles, 1 mole of an ideal solute dissolved in 1 kg of water will lower the vapor pressure by $1/(1 + 55.51)$ or 0.0177, i.e., by 1.77%. More conveniently, Raoult's law may be written

$$\frac{p}{p_o} = \frac{n_2}{n_1 + n_2} \quad (2)$$

indicating that, for the 1 molal solution, the vapor pressure is $55.51/(1 + 55.51)$ or 0.9823 or 98.23% of that of pure water. The ratio of the vapor pressures of solution and solvent is described by the term water activity (a_w),

$$a_w = \frac{p}{p_o} \quad (3)$$

so that the 1 molal solution referred to above has an a_w of 0.9823. An atmosphere in water vapor equilibrium with this solution will have a relative humidity of 98.23%. Thus, under equilibrium conditions, E.R.H. is equal to $a_w \times 100$. Provided that its vapor pressure is not reduced by interaction with insoluble materials, pure water has an a_w of 1.00, which is equivalent to an E.R.H. of 100%. The influence of water binding on a_w is discussed below.

The solutes of concern in foods are not ideal, and many will cause much greater depressions of vapor pressure and, hence, a_w than are predicted by Raoult's law. For nonelectrolytes, the difference may be small, at least up to 1 molal concentrations, but for electrolytes the effect is always great, increasing

TABLE 1.1.
Values of a_w for Aqueous Solutions
of 1 Molal Concentration

Solute	a_w
Ideal solute	0.9823
Glycerol	0.9816
Sucrose	0.9806
Sodium chloride	0.967
Calcium chloride	0.945

with the increase in the number of ions generated per molecule. Compare the a_w values for 1 molal solutions listed in Table 1.1. Thus, to calculate a_w values for nonideal solutes, a molal osmotic coefficient (ϕ) is used in the formula

$$\log_e a_w = \frac{-vm\phi}{55.51} \quad (4)$$

v is the number of ions generated by each molecule of solute and is equal to 1 for nonelectrolytes; m is the molal concentration. Values for ϕ are given by Robinson and Stokes (1955) for electrolytes, by Scatchard *et al.* (1938) for nonelectrolytes, and by Wolf (1966). Scott (1957) discusses the use of this formula. Tables of a_w and concentration for a range of solutes are given in Chapter 2.

Relative humidity has been widely used in mycology in the past to define the water relations of fungi, while physiologists have generally made reference to osmotic pressures in relevant studies of both plant and animal cells. As noted previously, these are less appropriate than a_w for the purpose. The relationship of a_w to E.R.H. has been mentioned; osmotic pressure may be converted to a_w by the expression

$$\text{Osmotic pressure} = \frac{-RT}{\bar{V}} \log_e a_w \quad (5)$$

where \bar{V} is the partial molar volume of water.

In such pure solutions as have been discussed above, the a_w differs from that predicted by Raoult's law primarily as a consequence of dissociation, where this occurs, and of interactions between solute molecules. In foods, as Karel (1973) points out, the situation is more complicated. Not all of the water is free to act as solvent, some being bound to specific groups of insoluble components. Additionally, some of the solutes also are bound to insoluble components. Thus, a knowledge of the water content of a food and the nature and amount of solutes present does not provide a basis for an accurate calculation of the food's a_w level.

WATER BINDING

The depression of water vapor pressure and, hence, a_w by the binding of water molecules in foods has received much attention. The most popular approach has been the Brunauer-Emmett-Teller (BET) isotherm of Brunauer *et al.* (1938), which, although derived from observations on nonpolar gases, gives very useful estimates of the size of the monolayer of adsorbed water molecules. Another approach utilizes measurements of the total heat of absorption of water as a function of a_w (Karel, 1973). Both techniques give indications of the level of hydration at which the mobility of small molecules becomes apparent and of the

total number of polar groups binding water. However, the greatest value in knowing the a_w at which the monolayer exists is that it appears to be the most stable water content for most foods. Lipid oxidation rates increase at water contents below the monolayer, while rates of nonenzymatic browning increase above it (Labuza, 1968).

The a_w may also be depressed by the capillary forces generated by water held within capillaries in foods. While knowledge of the dimensions of capillaries actually present in foods is meager, Karel (1973) suggests that capillaries with a radius of 10^{-6} cm are probably common, which would lead to definite capillary effects above an a_w level of 0.90. The capillarity of foods appears to play an important role also in the phenomenon of hysteresis, as will be discussed later.

WATER SORPTION ISOTHERMS

It will now be clear that the a_w of a food containing substantial amounts of insoluble constituents cannot be calculated accurately from a knowledge of the concentrations of the component solutes. It is necessary, therefore, to measure the a_w directly by methods outlined in Chapter 2. To obtain comprehensive data on the water relations of a food, the a_w levels corresponding to a range of water contents must be determined. These are plotted to provide a water sorption isotherm. This isotherm is useful, not only in showing at what water contents certain desirable or undesirable levels of a_w are achieved, but also in indicating what significance particular changes in water content will have in terms of a_w .

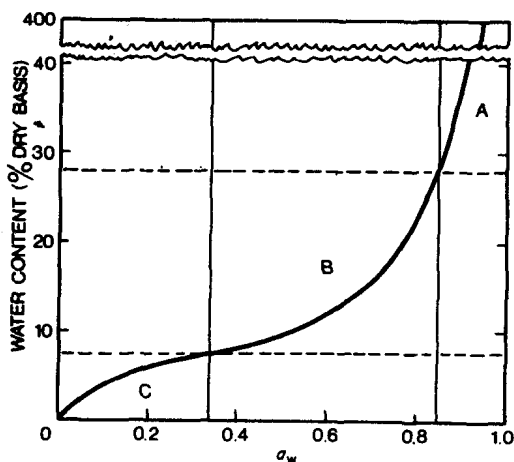


Fig. 1.1. A generalized water sorption isotherm of a typical food material. Regions A, B, and C are discussed in the text (Duckworth, 1974).

The schematic isotherm for a typical food material shown in Fig. 1.1 is taken from Duckworth (1974). The forces responsible for reducing the water vapor pressure are not the same throughout the range of a_w values, and A, B, and C on this isotherm represent regions in which different types of water binding may predominate.

As water is added to a dry food material, molecules are adsorbed onto appropriate sites until, statistically at least, all are occupied. This constitutes the water monolayer, formed in region C of the isotherm (Fig. 1.1). It is near the point of monolayer completion that given changes in water content have the most marked influence upon a_w . Conversely, relatively large changes in the a_w of the food are necessary to cause appreciable evaporation or condensation of water. The water of the monolayer (region C, Fig. 1.1) is thus very stable, behaving in many ways as part of the solid, and believed to be nonfreezable at any temperature (Duckworth, 1974). Foods that consist largely of soluble, low molecular weight components may have such a small monolayer that the relationship shown in region C of Fig. 1.1 does not occur.

The water in region B of the isotherm (Fig. 1.1) is less firmly bound than in the monolayer. Multilayer adsorption occurs, and the solution of soluble components becomes important, modified by the nature of insoluble solids present. The water in regions B and C differs markedly from "free" water, such as exists in region A. This latter, although mechanically trapped in the system, is subjected to only weak restrictive forces, as indicated by the steepness of the isotherm

TEMPERATURE EFFECTS

Note that the graphical relationships between water content and a_w are termed "isotherms." Changes in temperature affect the relation markedly, as is shown by the isotherms of raw chicken in Fig. 1.2 (Wolf *et al.*, 1973). Moreover, temperature gradients in a food material lead to water vapor pressure gradients, with resulting transfer of moisture and changes in a_w levels. The importance of such changes to the storage of foodstuffs is discussed in Chapter 10.

Many attempts have been made to formulate equations that will describe the temperature dependency of the isotherm. Most are very complex, involving the use of four constants. There is a simpler equation based on only two parameters (Iglesias and Chrife, 1976), which may be of more practical value, although it gives no indication of the physicochemical mechanism of water sorption.

HYSTERESIS

Temperature is not the only variable that can influence the amount of sorbed water in a food sample at a given a_w level. The water content will, for many

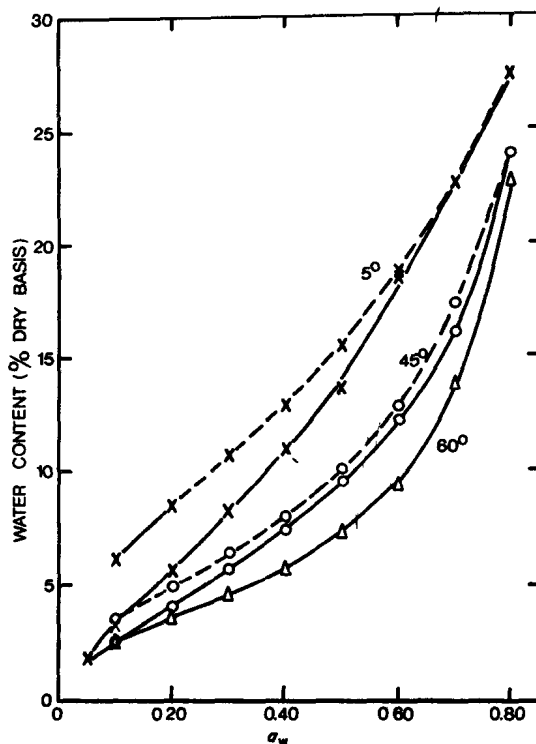


Fig. 1.2. Adsorption (—) and desorption (---) isotherms for raw chicken at three temperatures. Adsorption and desorption data were identical at 60°C (Wolf *et al.*, 1973)

foods, be higher when the a_w is achieved by desorption of water from a moist material than when the route is by adsorption to a dry food. This difference is termed hysteresis and is illustrated in Fig. 1.2 for raw chicken, in which it is greatest at 5°C and not detectable at 60°C.

A general sorption isotherm with regions as discussed by Labuza (1968) is shown in Fig. 1.3. This exaggerated hysteresis loop terminates near the a_w of monolayer formation, but, as mentioned earlier, the monolayer region A is not evident in all foods. Here region B is much narrower than region B of Fig. 1.1, and Labuza (1968) ascribes it to the adsorption of further layers of water on the monolayer. Region C of Fig. 1.3 is ascribed to condensation in pores (capillary effects), followed by dissolution of soluble components. This suggests that in this example hysteresis is a consequence predominantly of capillary condensation.

Thus, in theory, the course of water sorption by a dry material is first by the formation of a monolayer, followed by multilayer adsorption, the uptake into