

WATER in FOODS and BIOLOGICAL MATERIALS

*A
Nuclear
Magnetic
Resonance
Approach*

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PREFACE

Water is the most abundant substance on the earth and one of the most important components in foods and biological materials. The study of water has a long and distinguished history, along which came new ideas and new approaches. From natural phenomena, our ancestors learned how to preserve their foods by reducing the moisture content of the foods through wind and sun drying. These technologies are still being used by modern food and biological industries. In the late 1950's, a new concept regarding the properties of water was proposed by a British microbiologist named Scott. He believed that it was the "availability" of water, not the moisture content alone, that mattered and governed the deterioration of foods and biological materials. The term "water activity" or " a_w " as a measure of "availability" of water has since been used in many areas. Because the definition and measurement of water activity are based on thermal equilibrium, many scientists have questioned the use of water activity approach in systems that are not in the equilibrium state, which is the case for most of food and biological systems. In the late 1980's, Levine and Slade introduced the polymer science approach to food science, emphasizing the similarities between physiochemical properties of food biopolymers and synthetic polymers and the plasticizing effect of water. The

core issue of this approach is the glass-rubber transition process and glass transition temperature (T_g) in amorphous or partially crystalline substances. A material stored at a temperature below T_g is said to be physically, chemically, and biologically stable, while stored above T_g is not. The interaction between water and the solid material in the system is the most important factor governing T_g .

In this book, we have attempted to treat this long but still developing field by emphasizing new analysis methodology, data interpretation techniques, and illustrations of recent research results. We will start with a brief and easy-to-read introduction to the basic principles and techniques of nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI). The usefulness of the techniques in research and quality and process control in relation to water in foods and biological materials will also be addressed in the first chapter, and further demonstrated in more detail in the later chapters. In the second chapter, we will discuss the chemical structure and physical properties of the water molecule. In the subsequent five chapters, we will discuss recent development and research results in determination of water content and water migration; relationships between water mobility and physical, chemical and biological stability; and determination of glass transition temperature.

The intended audiences are personnel in academic institutes in the fields of food science and nutrition, food engineering, chemical engineering, pharmaceuticals, chemistry, physical chemistry, bioscience, medicine, particle science, and material science; and R&D personnel and managers in

food, pharmaceutical, bioproduct, cosmetic, and other industries. The book will also serve as a reference for students who want to get into this area or have interest in the study of water.

We are pleased to acknowledge those who assisted in the preparation of this book. We are grateful to Drs' Phil Perkins and Victor Huang who have read chapters and made useful comments. We would like to thank Victor Huang, Simon Almaer, Peter Pesheck, Phil Perkins, Hans Zoerb, Sumana Chakabarti, Quinghuang Geng, Daniel Fasold, Irwin Taub, Tom Yang, Hie-Joon Kim, Anne Bridges, Steven Leusner, Angela Ashton, Carlos Kantt, Dennis Zak, Ash Husain, Bruce Litchfield, Shelly Schmidt, Paul Lauterbur, Gary Fulcher, Joan Gordon, Ted Labuza, Susan Sun, Kehua Chang, Zhenzhong Long, Myong-soo Chung, Xiaoan Wang, Anrong Ning, Eric McEntyre, Jun Han, Suzy Zeng, Gi-Chul Jang, Cheng Zou, and many others who contributed to the experiment data and analyses used in the book. Specific thanks go to the people at the Center for Magnetic Resonance Research at the University of Minnesota directed by Dr. Kamil Ugurbil for the use of the MRI facility. Thanks also go to Anrong Ning for his assistance in preparation of cited references, and to Andrea Jahn for editorial assistance.

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Chapter 1. Nuclear Magnetic Resonance Techniques

1.1. Basic Principles of NMR

The concept that certain nuclei have an angular magnetic moment or spin was first postulated in 1924 by Wolfgang Pauli, but it was not until 1946 that the effect was first reported in bulk matter by groups led by Felix Bloch of Stanford University (Bloch, et al. 1946) and Edward Purcell of Harvard University (Purcell, et al. 1946). Their work laid the experimental foundations of nuclear magnetic resonance (NMR) spectroscopy, for which they were named co-recipients of the 1952 Nobel Prize in physics.

Any nucleus with a non-zero spin quantum number ($I \neq 0$), when placed in a magnetic field, can absorb and emit energy through electromagnetic radiation, which can be detected by NMR spectroscopy. Most of the elements in the Periodic Table have at least one isotope capable of nuclear magnetic resonance but there are a number of abundant isotopes such as ^{12}C , ^{16}O , ^{32}S , which have $I = 0$ and are not detected by NMR spectroscopy. The ^1H nucleus, especially the proton, is by far the most commonly used nucleus in NMR spectroscopy and NMR imaging or MRI (magnetic resonance imaging), primarily attributed to the ease of observation, its high natural abundance and the fact that it is invariably

present in the majority of samples, especially in biological samples. Besides ^1H , ^{13}C , ^{17}O , ^{19}F , ^{23}N , and ^{31}P , are also used in NMR studies because they are present in many compounds that interest medical and biological scientists.

1.1.1. Magnetic Moment and Magnetic Resonance

A nucleus with $I \neq 0$ is considered as spinning about an axis (Figure 1.1). The spinning generates a small magnetic field, which is called magnetic moment. Like a normal magnet bar, this magnetic moment has a north and a south pole, which is called nuclear magnetic dipole. When the nucleus is placed in a static magnetic field, it will interact with the field via its dipole, that is, the dipole will tend to align with the field much as a compass needle aligns with the Earth's magnetic field. In addition to this magnetic dipole, a second phenomenon occurs when the nucleus is placed in the static magnetic field. This can be demonstrated by considering the spinning nucleus as a spinning top. When the top is spun, it will spin but it begins to wobble when it slows down because of the presence of Earth's gravitational field. This wobbling or angular spinning is called precession. The spinning top is said to precess. Similarly, the spinning nucleus in a static magnetic field will precess about the static magnetic field. The frequency of precession of the nuclear dipole is called Larmor frequency (Abrabam 1960) defined by the Larmor equation

$$\omega = \gamma B_0 \quad (1.1)$$

where ω is the frequency of precession, B_0 is the strength of the static magnetic field, and γ is termed the gyromagnetic ratio and has a precise value characteristic of each nuclear species. For example, proton has an γ of 42.6 MHz/Tesla. If the static field B_0 is 1 Tesla, the ω is 42.6 MHz. If $B_0 = 4.7$ Tesla, the ω is about 200 MHz.

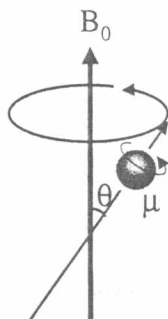


Figure 1.1. Magnetic moment precesses about the bulk magnetic field B_0 with an angle θ .

However, the orientations of magnetic dipoles in a static magnetic field (oriented in the z direction) are quantized according to quantum mechanic principles. This is referred to as “Zeeman splitting.” Each one of these orientations corresponds to a nuclear energy level

$$E = -\mu_z B_0 \quad (1.2)$$

where μ_z is the z component of the nuclear magnetic moment (z is the z axis of a Cartesian coordinate system, see 1.2.2.), which is defined by

$$\mu_z = m_I \gamma \hbar \quad (1.3)$$

where m_I is the nuclear magnetic quantum number, and \hbar is the Planck's constant divided by 2π . The m_I is characteristic of each nuclear energy level and takes the values

$$m_I = I, (I - 1), (I - 2), \dots, -(I - 2), -(I - 1), -I \quad (1.4)$$

The nuclear spin quantum number $I = \pm n/2$, where $n = 0, 1, 2, \dots$. For the hydrogen nucleus, the proton, with $I = \pm 1/2$, the magnetic quantum number m_I takes two values, i.e., $+1/2$ and $-1/2$. When placed in a static magnetic field, protons align themselves in either the same direction or in the opposite direction as the field depending on their magnetic quantum number. In the classic view described above, the alignment of the dipoles is determined by whether the nuclei precess in a clockwise or anti-clockwise direction. A nucleus that has its spin aligned with the field will have a lower energy than when it has its spin aligned in the opposite direction to the field (Figure 1.2).

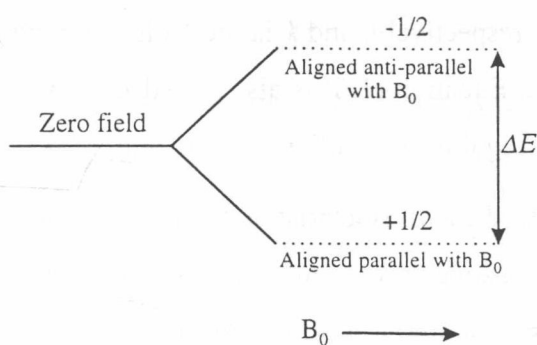


Figure 1.2. Nuclear Zeeman splitting of energy levels in a magnetic field for spins with quantum number $1/2$.

Since a lower energy state is more stable than a higher energy state, there are more nuclei in the lower level than in the upper level. The population difference between the upper and lower levels is very small – one out of every million dipoles. However, it is this small population difference that is used in NMR spectroscopy. The energy difference ΔE is proportional to the strength of the static field and the population difference

$$\Delta E = \gamma \hbar B_0 \quad (1.5)$$

and

$$\frac{N_{upper}}{N_{lower}} = e^{-\Delta E/kT} \quad (1.6)$$

where N_{upper} and N_{lower} represent the population of nuclei in the upper and lower energy levels, respectively, and k is the Boltzmann constant and T is absolute temperature. Equation (1.6) is also called Boltzmann's law, which describes the thermal equilibrium of the nuclear spins.

Having discussed the characteristics of magnetic moment in a static field, let's talk about magnetic resonance, the basic principles of NMR. The NMR experiment is to induce transition between the neighboring energy levels by absorption or emission of a photon with the requisite energy. This requisite energy is applied in the form of a rotating magnetic field B_1 or *radio frequency* (RF) pulse, whose frequency exactly matches the Larmor

frequency, and whose energy is equal to the ΔE , and causes resonant absorption or emission of the energy by the nuclei. This resonance effect is therefore termed *nuclear magnetic resonance*. This particular frequency is termed resonance frequency which is governed by the Bohr condition

$$\Delta E = h\nu \quad (1.7)$$

where h is the Planck's constant and ν is the resonance frequency. From Equation (1.5) and (1.7) we have the famous Larmor equation

$$\nu = \gamma B_0 / 2\pi \quad (1.8)$$

Therefore, for any particular nucleus in a given static magnetic field B_0 , the NMR frequency, also termed as Larmor frequency, will be characteristic primarily of the gyromagnetic ratio γ peculiar to that particular nucleus.

The resonant absorption or emission of energy causes both upward and downward transition of the nuclear spins. Because there is a greater spin population in the lower energy level, there will be more upward transitions than downward transitions, resulting in a nonequilibrium spin distribution. If this process continues, the excess of nuclei in the lower energy level will continually diminish. Under certain circumstances the two spin populations