ADVANCES IN EXPERIMENTAL MEDICINE AND BIOLOGY

Volume 302

WATER RELATIONSHIPS IN FOODS

Advances in the 1980s and Trends for the 1990s

Edited by Harry Levine
and Louise Slade

WATER RELATIONSHIPS IN FOODS

Advances in the 1980s and Trends for the 1990s

Edited by

Harry Levine

Senior Principal Scientist
Nabisco Brands, Inc.
East Hanover, New Jersey

and

Louise Slade

Research Fellow
Nabisco Brands, Inc.
East Hanover, New Jersey

PLENUM PRESS • NEW YORK AND LONDON

Library of Congress Cataloging in Publication Data

Water relationships in foods: advances in the 1980s and trends for the 1990s / edited by Harry Levine and Louise Slade.

p. cm.—(Advances in experimental medicine and biology; v. 302)

"Based on the American Chemical Society symposium on water relationships in foods, held April 10–14, 1989 in Dallas, Texas"—T.p. verso.

Includes bibliographical references and index.

ISBN 0-306-43936-0

1. Food—Water activity—Congresses. 2. Food—Moisture—Congresses. I. Levine, Harry, 1947- . II. Slade, Louise. III. American Chemical Society. IV. Series.

TX553.W3W38 1991 91-21416

664—dc20 CIP

Proceedings based on the American Chemical Society symposium on Water Relationships in Foods, held April 10–14, 1989, in Dallas, Texas

ISBN 0-306-43936-0

Printed in the United States of America

WATER RELATIONSHIPS IN FOODS

Advances in the 1980s and Trends for the 1990s

ADVANCES IN EXPERIMENTAL MEDICINE AND BIOLOGY

Recent Volumes in this Series

Volume 295
THE BASAL FOREBRAIN: Anatomy to Function
Edited by T. Celeste Napier, Peter W. Kalivas, and Israel Hanin

Volume 296
PLASTICITY AND REGENERATION OF THE NERVOUS SYSTEM
Edited by Paola S. Timiras, Alain Privat, Ezio Giacobini, Jean Lauder, and Antonia Vernadakis

Volume 297
NEW ASPECTS OF HUMAN POLYMORPHONUCLEAR LEUKOCYTES
Edited by W. H. Hörl and P. J. Schollmeyer

Volume 298
SENSORY NERVES AND NEUROPEPTIDES IN GASTROENTEROLOGY: From Basic Science to Clinical Perspectives
Edited by Marcello Costa, Calogero Surrenti, Sergio Gorini, Carlo Alberto Maggi, and Alberto Meli

Volume 299
ADVANCES IN PERINATAL THYROIDOLOGY
Edited by Barry B. Bercu and Dorothy I. Shulman

Volume 300
MECHANISMS AND SPECIFICITY OF HIV ENTRY INTO HOST CELLS
Edited by Nejat Düzgünes

Volume 301
MECHANISMS OF ANESTHETIC ACTION IN SKELETAL, CARDIAC, AND SMOOTH MUSCLE
Edited by Thomas J. J. Blanck and David M. Wheeler

Volume 302
WATER RELATIONSHIPS IN FOODS: Advances in the 1980s and Trends for the 1990s
Edited by Harry Levine and Louise Slade

A Continuation Order Plan is available for this series. A continuation order will bring delivery of each new volume immediately upon publication. Volumes are billed only upon actual shipment. For further information please contact the publisher.

PREFACE

This book was developed from the papers presented at a symposium on "Water Relationships in Foods," which was held from April 10-14, 1989 at the 197th National Meeting of the American Chemical Society in Dallas, Texas, under the auspices of the Agricultural and Food Chemistry Division of ACS. The editors of this book organized the symposium to bring together an esteemed group of internationally respected experts, currently active in the field of water relationships in foods, to discuss recent advances in the 1980's and future trends for the 1990's. It was the hope of all these contributors that this ACS symposium would become a memorable keystone above the foundation underlying the field of "water in foods." This strong foundation has been constructed in large part from earlier technical conferences and books such as the four milestone International Symposia on the Properties of Water (ISOPOW I-IV), the recent IFT Basic Symposium on "Water Activity" and Penang meeting on Food Preservation by Moisture Control, as well as the key fundamental contributions from the classic 1980 ACS Symposium Series #127 on Water in Polymers, and from Felix Franks' famous seven-volume Comprehensive Treatise on Water plus five subsequent volumes of the ongoing Water Science Reviews. The objective of the 1989 ACS symposium was to build on this foundation by emphasizing the most recent and major advances in the field and stressing the new research concepts and developments which have been seen to gather momentum in the decade of the 1980's and promise the potential of useful and routine technological applications in the 1990's. This book represents the realization of that objective.

Over the course of 9 half-day sessions in Dallas, 45 invited speakers from industry and academia in the USA (28), Europe (13), Canada (2), and Japan (2) delivered presentations on current research on water in foods and food-related materials such as pharmaceuticals and cryobiologicals. The sections of this book have been organized according to the central themes (described below) of each of the half-day sessions. All but three of the invited speakers agreed to contribute chapters to the book. A few additional chapters were contributed by other participants at the symposium. In testimony to the widespread interest in this important subject area of modern food science and technology, the recognized scientific quality of the work of the invited speakers, and the depth and breadth of the meeting program, the symposium attracted an extraordinary level of food-industry support from 20 major international corporate sponsors (acknowledged below).

A valuable feature of the symposium program was an hour-long open forum with a different leader presiding at the end of each day's sessions, to discuss the presentations of the day and a previously circulated list of topics, and much of the gist of these discussions has been incorporated by many of the chapter authors in their written manuscripts. During these lively exchanges and sometimes controversial debates, questions from the audience and a panel of speakers were aimed at a critical evaluation of the new vs. old concepts, approaches, and experimental methods in the field of water in foods. Advocates of new concepts and approaches emphasized the significance of glassy and rubbery behavior and glass transitions in foods, the non-equilibrium nature of "real world" food products and processes, the appropriate use of kinetics rather than energetics, the value of a polymer or materials science approach to describe the effect of water as a plasticizer on the glass transition temperature, cryostabilization technology, and the utility of dynamics maps (state diagrams modified to introduce kinetics) in understanding the effects of diffusion-limited relaxation processes and their kinetics on food product quality, stability, safety, and technological performance. Some of these advocates were on a mission (which they have continued to pursue via this book) to dispel old "myths" and "slaughter some sacred cows," including the treatment of systems having practically finite dilution with such traditional concepts and approaches as "water activity," "bound water," "water binding capacity," "equilibrium" water vapor sorption isotherms and related theories and equations derived from equilibrium thermodynamics, "BET monolayer" values, and multiple "states" of liquid water. Advocates of the more traditional approaches defended (at the symposium, and also in this book) the practical utility of the established concepts (within their recognized limitations) and were skeptical about the widespread relevance of the new conceptual approaches to complex (as opposed to model) food systems. A larger block of undecided participants acknowledged the absence of universal applicability and predictive capability of the conventional approaches, but had been trained in their use and lacked alternatives. Some in this group were aware of the new perspectives and interpretations, and so came to the symposium open-minded, albeit sometimes confused by seeming controversies in the literature, frequently arising from questions of semantics or nomenclature, or differences in the time scales relevant to various experimental measurement methods (e.g. differential scanning calorimetry and thermomechanical analysis, nuclear magnetic resonance, electron spin resonance spectroscopy). The aim of the symposium was not to solve all problems or resolve all contentious issues in the areas of water relationships and moisture management in foods, but rather to air and assess different viewpoints, in the context of interpretations of current research findings. This book is faithful to that aim.

An illustration of the current state of affairs surrounding the traditional "water activity" approach is worth mentioning. A 1989 Institute of Food Technologists expert panel on food safety and nutrition recently ranked "the concept of water activity (which created a greater understanding of why food spoils)" as one of the top ten food-science innovations of the last 50 years! At the same time, in the Foreword to the book entitled "Food Preservation by Moisture Control" (C. C. Seow, ed., Elsevier Applied Science, London (1988)), R. B. Duckworth (President, ISOPOW Executive Committee) wrote: "Those more immediately involved in practical aspects of methods of food preservation which depend for their effectiveness on control of the aqueous environment within a material must remain alive to the fact that newer research is currently leading to important changes in our understanding of the properties of water in foods, and that some previously widely-held views on the theoretical background to their activities are no longer tenable. At the same time, methods such as the measurement of relative water vapour pressure (a_w) which have long been used for characterizing the state of water in foods and which continue to prove empirically highly useful, should still be exploited to their fullest advantage, yet with a greater appreciation of their theoretical limitations."

Editors' note - As a matter of editorial policy, and for the purposes of consistency and rigor throughout this book, certain words (commonly used throughout the literature on water in foods) appear with or without quotation marks, depending on how they are used. For example, the term *water activity* (without quotation marks) is only used to describe rigorously appropriate cases of infinitely dilute systems at equilibrium. The word *states* (without quotation marks) is only used to describe physical (solid, liquid, gas) or structural (crystalline, amorphous) states of matter. In all other instances, quotation marks are used to denote colloquial usage of words such as "water activity" (signifying relative vapor pressure), "states" (signifying different conditions or extents of mobility of liquid water), and "bound" (or "binding") or "free" (signifying hindered or unhindered mobility of water, respectively).

The symposium began with a keynote address by Prof. Felix Franks on the subject of new perceptions of water relationships in foods (chapter 1). It will come as no surprise to many readers of this book to learn that Prof. Franks attempted to dispel as many old myths and slaughter as many sacred cows as one could in a 1-hour lecture. His talk set the tone for the first day, which included presentations within the themes of "New Directions" and "Thermal Analysis Approach" by several of his former collaborators (L. Slade and H. Levine, D. Reid, T. Schenz, and T. Maurice). The chapters based on these talks emphasize aspects of the non-equilibrium behavior of aqueous food systems in glassy and rubbery states, including frozen systems relevant to the field of cryotechnology. These chapters describe various experimental approaches used in these studies, as well as the new interpretive (as distinguished from theoretical) approaches employed to develop a deeper qualitative understanding of the experimental results obtained. The chapters based on subsequent talks by M. Le Meste, D. Simatos, and M. Karel on aspects of diffusion and mobility in aqueous food systems attempt to counterbalance the perspective and interpretations of Franks and his co-workers with alternative viewpoints on a number of contentious issues. As should become obvious to the reader after examining the first two sections of this book, these presentations succeeded in generating much debate and stimulating much greater depth in exchanges of ideas during the discussion periods throughout the duration of the symposium.

The second day was devoted to the themes of "Water Activity" and Water Sorption Studies (covered in the third and fourth sections of this book). Featured presenters on the former theme included T. Labuza and T. Lilley, and on the latter, H. Weisser. The chapter based on Lilley's presentation is distinguished by the only appropriate use of the term *water activity* to describe aqueous systems in the limit of infinite dilution. All other oral references to "*water activity*" were constructively amended or replaced by the term *relative vapor pressure* with increasing frequency as the day and week progressed. Similarly, the term "*bound water*" may finally have been laid to rest and replaced (or at least amended) by more appropriate references to the hindered mobility of water in the presence of any water-compatible or water-sensitive solute. The development of a consensus on these issues helped to justify the above-mentioned editorial policy on nomenclature adopted throughout this book. The highlight of the third day (theme: "Technological Advances" - section six) was a presentation by I. Tomka on the structural and thermodynamic properties of hydrophilic polymer-water systems. Other featured speakers included J. Blanshard, S. Ablett, and J. Flink. The fourth day was devoted entirely to the NMR "afficianados" and began with an excellent introductory overview of NMR theory and practice by S. Schmidt, the written version of which constitutes the lead-off chapter of the NMR section (five) of this book. Chapters based on several subsequent talks deal with NMR analyses of aqueous carbohydrate, protein, or flour/dough systems. The exciting potential use of magnetic resonance imaging to study the spacial and phase distributions of water in foods is described in the chapter by M. McCarthy and co-workers. The ninth session had a theme of "Structural Studies" (section seven) and featured talks on the molecular dynamics simulation of aqueous small sugars (J. Brady), X-ray analyses of polysaccharides (R. Chandrasekaran and R. Millane), and compressibility studies on globular protein solutions (K. Gekko). The final discussion period was ably led by C. van den Berg, who included in some informal remarks a brief but cogent synopsis and thoughtful assessment of what were to him the highlights and shortcomings of the symposium's previous discussions. Van den Berg's overview appears as chapter 2.

By all accounts, the symposium was a great success. For example, R. Duckworth (an invited guest of special distinction, as the pioneer of the original ISOPOW in 1974) described the Dallas symposium as "an important and truly valuable meeting...a milestone...which provided an interesting and potentially valuable new way of looking at the influences of water on food quality" (ISOPOW Newsletter 3, Aug. 1, 1989). Excellent overviews and stimulating presentations of "state of the science" research and experimental methodology elicited much constructive and productive discussion (the highlights of which have been incorporated in many of the chapters). This led to progress by those on both sides of controversial issues toward a compromise recommendation to appreciate and utilize in a combined approach the best of the old and new concepts (see, e.g., van den Berg's chapter 2). L. Slade (chapter 3) illustrated one such compromise with an analysis of three-dimensional (i.e. temperature, moisture content, time) sorption isotherms superimposed on a glass curve for a given substrate-water system. Another consensus recommendation concerned analyses of glass transitions (or other relaxation processes coinciding with the onset of system mobility) by multiple experimental methods, with special attention paid to the time-dependence of such relaxations.

The proposal and outline for this book of symposium proceedings received many remarkably favorable comments from a large collection of external peer reviewers (commissioned by ACS) from the field of food science and technology. In fact, despite the many well-known books (mentioned above) previously published on this and related subjects, many of the reviewers expressed the shared opinion that this book is much needed by food scientists, because there are no other publications similar or comparable to it, with respect to the quality, breadth, and extreme thoroughness of its coverage, which is at the same time also focused, cohesive, and coherent. More than one reviewer went on to say that this book will fill a gap in the literature; it presents a new viewpoint on an old topic, and a focus on newer ways of treating older concepts about the "state" of water in food materials. We hope that its readers judge that this product has lived up to its promise.

ACKNOWLEDGEMENTS

The financial support (which assisted 18 of the 45 invited speakers to attend the meeting) and encouragement from the following international food-industry corporate sponsors of the Dallas ACS symposium are gratefully acknowledged:

Quaker Oats
Nestle SA
United Biscuits
Kraft
Miles
National Starch & Chemical
A. E. Staley
Unilever
Borden
Campbell Soup
Frito-Lay
Keebler
Thomas J. Lipton
Nabisco Brands
Warner-Lambert
Allied Lyons
Ross Laboratories
American Maize-Products
Grain Processing
Uncle Ben's

The official sponsorship, financial support, and assistance in the arrangements for the symposium by the Agricultural and Food Chemistry Division of the American Chemical Society, and the cooperation of its officers, M. Phillips, C. J. Mussinan, and J. W. Finley, are also gratefully acknowledged.

The editors wish to give special thanks to all the invited speakers, whose contributions and assistance made possible the ACS Symposium on Water Relationships in Foods and the publication of its proceedings in this book. We thank them sincerely, and their many chapter co-authors as well, for all their invaluable efforts on behalf of this book, and especially for their hard work, diligence, perseverance (throughout the process of creating this book, which began in January, 1988), and cooperation. The latter was particularly noteworthy in light of the unusually rigorous editorial policies (both technical and copy-) imposed on them by us, which necessitated a great deal of time-consuming revisions of chapter drafts, in order to ensure the highest possible attention to technical quality, as well as readability and consistency of style and format, throughout this book. In almost all cases, our admittedly heavy-handed editorial tactics were borne with much grace. We hope that the readers of this book will judge themselves to be the ultimate beneficiaries.

Last, but not least, we acknowledge a huge debt of gratitude to Mrs. Jane Korbett, who single-handedly carried out the central retyping into camera-ready format of every single page of this mammoth book. We thank her sincerely for her remarkable dedication to this enormous and seemingly never-ending project, and for the excellence of her work.

Harry Levine and Louise Slade

CONTENTS

NEW DIRECTIONS

THERMAL ANALYSIS APPROACH

TECHNOLOGICAL ADVANCES

STRUCTURAL STUDIES

HYDRATION PHENOMENA: AN UPDATE AND IMPLICATIONS FOR THE FOOD PROCESSING INDUSTRY

Felix Franks

Biopreservation Division, Pafra Ltd.
150 Cambridge Science Park, Cambridge CB4 4GG, U.K.
and Girton College, Cambridge

ABSTRACT

The past decade has witnessed major revisions in our perception of the manner in which water affects the physical, chemical, and microbiological attributes of all manner of food-related systems. The growing realization that, during processing, most such systems are brought to, and maintained in, a state of thermodynamic instability is focussing attention on the dynamics of the various components in such systems. Older, equilibrium-based concepts, such as "water activity," equilibrium moisture sorption, and "bound" water are being discarded in favour of more appropriate descriptions, in terms of diffusion, nucleation, crystallization and relaxation rates, glass/rubber transitions, and steady states. It is being realized that food processing, materials science, and polymer technology have much in common, with water being the universal plasticizer of naturally occurring organic materials which form the basis of food products.

INTRODUCTION

Studies of water relationships of foods have a long and distinguished history. The subject received an impetus following the growth and diversification of the food processing industries and the search for products of superior quality and longer shelf lives. Since water is usually a major, and frequently the major, component of food products, its role in determining safety, quality, texture, and other attributes is clearly of some importance. With the focus on water, food products can be grouped under three major headings, as shown in Table 1.

Early on, the water content of a given product was thought to be the critical factor in the control of microbial growth and other properties. Scott first suggested that the water activity, A_w, provided a better and more reliable measure.[1] Since then, A_w has come to be universally adopted as the determining factor for safety and quality, despite certain reservations which have been voiced from time to time.[2]

The book Water Relations of Foods,[3] containing the proceedings of a conference, held in 1974 at the University of Strathclyde, was a milestone in the progress to a better understanding of how water interacts with food components and how such interactions determine the attributes of food com-

Water Relationships in Food, Edited by H. Levine and L. Slade, Plenum Press, New York, 1991

Table 1. Classification of food products according to water content and type of appropriate physico-chemical approach.

Physical state	Product examples	Physico-chemical treatment
Dilute solutions/ dispersions	Drinks, soups	Equilibrium thermodynamics, refer to Henry's law
Semi-dilute solution/ dispersion (high moisture content)	Purees, jellies	Polymer chemistry, chain entanglement, sol-gel transformations
Solids (high moisture)	fish, vegetable, meat, ice cream	Biophysical chemistry, colloid science
(intermediate moisture)	preserves, sausages	Materials science
(low moisture)	dried products, cereals	Materials science, glass/ rubber transitions

posites. However, during the past 15 years, any further major advances that might have been made have not yet come to be generally accepted by the industry and the legislators who frame food safety regulations. This lack of progress is remarkable when set against major developments, both experimental and theoretical, in studies of aqueous solutions, dispersions, gels, ice, and the hydration behaviour of ions, simple molecules, and macromolecules.[4]

It is the purpose of this introductory chapter to examine whether recent progress in studies of aqueous systems in general can usefully be applied to gain a better understanding of, and better control over, processes relevant to the food industry.

MICROSCOPIC AND MACROSCOPIC INFORMATION

Considerable progress has been made in the elucidation of the interactions of water with ions and molecules in solution. Most of it is of a microscopic (molecular) nature and describes the behaviour of individual water molecules, as influenced by the electrostatic fields surrounding ions, or by direct hydrogen bonds to polar sites on organic molecules, such as carbohydrates. Particular progress has been made in our understanding of hydrophobic effects,[5] and attempts are currently under way to develop a comprehensive description of the various hydration effects, in efforts to express hydration and *in vitro* stabilities of biological macromolecules.

The development of computer simulation methods has contributed significantly to the advancement of an understanding of hydration phenomena at the molecular level. Basic to such studies is the form of the water dimer potential function employed in the calculations. Altogether, more than 20 water dimer potential functions have been proposed since 1970, all of which can correctly account for either the behaviour of water dimer (vapour) or of liquid water, but not both.[6] None can fit the properties of the liquid over the whole temperature range.

As regards novel experimental techniques, the development of molecular beam scattering techniques has enabled physicists to obtain experimental water dimer potential functions, just as neutron diffraction by liquids has led to important developments in the study of liquid water and aqueous electrolyte solutions.[7]

Probably the most significant development in experimental techniques is in n.m.r. The combination of high-field, stable magnets and computer simulation methods has made possible the detailed study of time-averaged structures and dynamics of complex molecules in the liquid and solid states. The application of such procedures to carbohydrates in solution will serve as a good illustration.

HYDRATION AND CONFORMATIONS OF SMALL CARBOHYDRATES

For many years, sugars have been the Cindarellas of solution physical chemistry. They were deemed to be of little interest because of the almost ideal behaviour of their aqueous solutions.[9] They possess no chromophores in the easily accessible spectral range, and the results from optical activity measurements are not easily translated into molecular detail.[10] The advent of advanced n.m.r. techniques, coupled with the availability of computing facilities, has provided a new stimulus to studies of small carbohydrates in solution. A further impetus has come from the realization of the important biological functions of oligosaccharides linked to polypeptide chains.[11]

Figure 1 shows a high resolution proton n.m.r. spectrum of a reasonably simple molecule, sorbitol.[12] From such spectra, it is now possible to extract information about molecular conformation and flexibility, and it has been shown that both these attributes are affected differently by different solvents.

One of the most important results to emerge from recent studies of carbohydrates in solution is the realization that, in contrast to proteins, the solution conformations and molecular shapes differ markedly from those in the crystalline states.[13] Extrapolations from crystal structures to amorphous states, anhydrous or hydrated, must therefore be treated with great caution.[14]

The combination of spectral data with computer simulation now enables molecular conformation and hydration to be probed. Figure 2 shows the "hydration structures" and hydration dynamics of sorbitol and mannitol.[15] Curiously, the simulation results suggest that the water molecule residence times in the hydration shells are shorter than those of water molecules in the bulk liquid. In terms of conventional definitions, the sugar alcohols (and sugars) would thus be classified as structure breakers, but see below.

The wealth of molecular detail which is gradually becoming available clearly demonstrates that earlier theoretical treatments of carbohydrate solutions in terms of simple hydration equilibria and hydration numbers (bound water) are quite inappropriate and nothing better than procedures for fitting experimental data.[16] It has also become clear that the apparent ideal solution (Henry's law) behaviour of sugar solutions originates from the fact that the heats of solution (which are not equal to zero, as would be demanded by ideal mixing) are almost completely compensated by the entropies, thus leaving $\Delta G \approx 0$ (pseudo ideal).[9] What is also becoming clear is that anomeric, tautomeric, and conformational equilibria involving sugar molecules are very sensitive to stereochemical detail,[17] and that solvent interactions play a decisive part in determining the compositions of anomeric and tautomeric equilibrium mixtures.[18] Arguably, such solvent contributions to sugar behaviour are more important than they are for peptides or