Cereals in Breadmaking

A Molecular Colloidal Approach

Ann-Charlotte Eliasson
Kåre Larsson

Food Technology
Chemical Center
University of Lund
Lund, Sweden

Marcel Dekker, Inc. New York • Basel • Hong Kong

Library of Congress Cataloging-in-Publication Data

Eliasson, Ann-Charlotte.
Cereals in breadmaking : a molecular colloidal approach / Ann-Charlotte Eliasson, Kåre Larsson.
p. cm. — (Food science and technology ; 55)
Includes bibliographical references and index.
ISBN 0-8247-8816-8
1. Bread—Analysis. 2. Grain—Analysis. 3. Colloids.
I. Larsson, Kåre, . II. Title. III. Series: Food science and technology (Marcel Dekker, Inc.) : 55.
TX558.B7E45 1993
664'.752—dc20 92-40313
CIP

This book is printed on acid-free paper.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Cereals in Breadmaking

', Mi-

rt C.

Ting

Rizvi
Kare

How-

sella

r

illips

n A.

Ruth

h H.

dited

and

Lees

Kåre

and

lited

Karel

eon

d R.

rse

FOOD SCIENCE AND TECHNOLOGY

A Series of Monographs, Textbooks, and Reference Books

1. Flavor Research: Principles and Techniques, *R. Teranishi, I. Hornstein, P. Issenberg, and E. L. Wick*
2. Principles of Enzymology for the Food Sciences, *John R. Whitaker*
3. Low-Temperature Preservation of Foods and Living Matter, *Owen R. Fennema, William D. Powrie, and Elmer H. Marth*
4. Principles of Food Science
   Part I: Food Chemistry, *edited by Owen R. Fennema*
   Part II: Physical Methods of Food Preservation, *Marcus Karel, Owen R. Fennema, and Daryl B. Lund*
5. Food Emulsions, *edited by Stig E. Friberg*
6. Nutritional and Safety Aspects of Food Processing, *edited by Steven R. Tannenbaum*
7. Flavor Research: Recent Advances, *edited by R. Teranishi, Robert A. Flath, and Hiroshi Sugisawa*
8. Computer-Aided Techniques in Food Technology, *edited by Israel Saguy*
9. Handbook of Tropical Foods, *edited by Harvey T. Chan*
10. Antimicrobials in Foods, *edited by Alfred Larry Branen and P. Michael Davidson*
11. Food Constituents and Food Residues: Their Chromatographic Determination, *edited by James F. Lawrence*
12. Aspartame: Physiology and Biochemistry, *edited by Lewis D. Stegink and L. J. Filer, Jr.*
13. Handbook of Vitamins: Nutritional, Biochemical, and Clinical Aspects, *edited by Lawrence J. Machlin*
14. Starch Conversion Technology, *edited by G. M. A. van Beynum and J. A. Roels*
15. Food Chemistry: Second Edition, Revised and Expanded, *edited by Owen R. Fennema*

16. Sensory Evaluation of Food: Statistical Methods and Procedures, *Michael O'Mahony*
17. Alternative Sweetners, *edited by Lyn O'Brien Nabors and Robert C. Gelardi*
18. Citrus Fruits and Their Products: Analysis and Technology, *S. V. Ting and Russell L. Rouseff*
19. Engineering Properties of Foods, *edited by M. A. Rao and S. S. H. Rizvi*
20. Umami: A Basic Taste, *edited by Yojiro Kawamura and Morley R. Kare*
21. Food Biotechnology, *edited by Dietrich Knorr*
22. Food Texture: Instrumental and Sensory Measurement, *edited by Howard R. Moskowitz*
23. Seafoods and Fish Oils in Human Health and Disease, *John E. Kinsella*
24. Postharvest Physiology of Vegetables, *edited by J. Weichmann*
25. Handbook of Dietary Fiber: An Applied Approach, *Mark L. Dreher*
26. Food Toxicology, Parts A and B, *Jose M. Concon*
27. Modern Carbohydrate Chemistry, *Roger W. Binkley*
28. Trace Minerals in Foods, *edited by Kenneth T. Smith*
29. Protein Quality and the Effects of Processing, *edited by R. Dixon Phillips and John W. Finley*
30. Adulteration of Fruit Juice Beverages, *edited by Steven Nagy, John A. Attaway, and Martha E. Rhodes*
31. Foodborne Bacterial Pathogens, *edited by Michael P. Doyle*
32. Legumes: Chemistry, Technology, and Human Nutrition, *edited by Ruth H. Matthews*
33. Industrialization of Indigenous Fermented Foods, *edited by Keith H. Steinkraus*
34. International Food Regulation Handbook: Policy · Science · Law, *edited by Roger D. Middlekauff and Philippe Shubik*
35. Food Additives, *edited by A. Larry Branen, P. Michael Davidson, and Seppo Salminen*
36. Safety of Irradiated Foods, *J. F. Diehl*
37. Omega-3 Fatty Acids in Health and Disease, *edited by Robert S. Lees and Marcus Karel*
38. Food Emulsions: Second Edition, Revised and Expanded, *edited by Kåre Larsson and Stig E. Friberg*
39. Seafood: Effects of Technology on Nutrition, *George M. Pigott and Barbee W. Tucker*
40. Handbook of Vitamins: Second Edition, Revised and Expanded, *edited by Lawrence J. Machlin*
41. Handbook of Cereal Science and Technology, *Klaus J. Lorenz and Karel Kulp*
42. Food Processing Operations and Scale-Up, *Kenneth J. Valentas, Leon Levine, and J. Peter Clark*
43. Fish Quality Control by Computer Vision, *edited by L. F. Pau and R. Olafsson*
44. Volatile Compounds in Foods and Beverages, *edited by Henk Maarse*

Instrumental Methods for Quality Assurance in Foods, *edited by Daniel Y. C. Fung and Richard F. Matthews*

Listeria, Listeriosis, and Food Safety, *Elliot T. Ryser and Elmer H. Marth*

Acesulfame-K, *edited by D. G. Mayer and F. H. Kemper*

Alternative Sweeteners: Second Edition, Revised and Expanded, *edited by Lyn O'Brien Nabors and Robert C. Gelardi*

Food Extrusion Science and Technology, *edited by Jozef L. Kokini, Chi-Tang Ho, and Mukund V. Karwe*

Surimi Technology, *edited by Tyre C. Lanier and Chong M. Lee*

Handbook of Food Engineering, *edited by Dennis R. Heldman and Daryl B. Lund*

Food Analysis by HPLC, *edited by Leo M. L. Nollet*

Fatty Acids in Foods and Their Health Implications, *edited by Ching Kuang Chow*

Clostridium botulinum: Ecology and Control in Foods, *edited by Andreas H. W. Hauschild and Karen L. Dodds*

Cereals in Breadmaking: A Molecular Colloidal Approach, *Ann-Charlotte Eliasson and Kåre Larsson*

Low-Calorie Foods Handbook, *edited by Aaron M. Altschul*

Additional Volumes in Preparation

Antimicrobials in Foods: Second Edition, Revised and Expanded, *edited by P. Michael Davidson and Alfred Larry Branen*

Preface

Bread has a unique status among foods based on its long history in all parts of the world. It is not surprising that in many languages the word for bread means foods in general, as we know from the Bible. The science of breadmaking is a challenge in food research. There is scarcely any other type of food in which the progression of changes from the initial raw material to the final product is more complicated. It is also remarkable that this art was refined to perfection thousands of years ago, without any knowledge of the chemistry, physics, or microbiology involved.

The effort to understand the chemistry of the baking process has a relatively short history. When the nature of proteins was revealed through work by The Svedberg and others, it became possible to study wheat proteins, aqueous gel properties fractions of wheat flour components. Remarkable achievements were reported by Haugaard and Johnson in 1930. Their work deserves particular attention among earlier studies, as being the first attempt at a colloidal point of view.

Research over the last three decades has explained many of the unique properties of wheat storage proteins, which in turn determine the baking properties of wheat flour. Most recent studies have focused on separation and characterization of these proteins and, in particular, relating protein quality to breadmaking performance. This is certainly one important piece of information needed to provide a general basis for plant breeding with baking performance and bread quality in mind. A long-neglected field of knowledge, however, is the surface and colloid chemistry involved in the wheat flour–water interaction—from dough mixing until fixation of the bread structure in connection with the starch gelatinization in the oven. Colloid science is in fact the only discipline that provides the tools to describe this process completely; if we try to understand these phenomena only through chemical/analytical knowledge of all the components, we can't see the forest for the trees.

Our laboratory has applied a colloidal approach to bread technology. New results are presented in this volume on the gluten structure in bulk and at interfaces, on phase separation in the dough, and on the transition from a foam to a pore system. On the basis of these results and recent progress in the understanding of shape in biomolecular assemblies derived from forces and curvature at interfaces, it is possible to present a complete structural model of the breadmaking process. As a background to this model it was natural to review the present molecular and colloidal knowledge of the chain from wheat grain to bread. As an introduction, the basic concepts of colloid science are presented with a minimum of theory.

The scientific literature on breadmaking is concentrated in journals and textbooks on cereals. Wheat is by far the most important crop for breadmaking and is given the most coverage in this book. We have included research on oats, rye, maize, and other grains in Chapters 4 and 7.

Bread research in our department started in about 1975 with a Ph.D. thesis by T. Carlson, supervised by one of us (K. Larsson), which was followed by many others. We are grateful for these contributions and to the Swedish Council for Forestry and Agricultural Research and to the Cerealia Foundation R&D, Stockholm, for supporting the cereal research in our department.

This volume is intended to be a useful textbook for advanced studies in cereal technology. We also hope the book will be read by scientists active in cereal research world-wide.

Ann-Charlotte Eliasson
Kåre Larsson

Contents

1

Basic Concepts of Surface and Colloid Chemistry

I. INTRODUCTION

An ordinary light microscope can be used to study particles down to micrometer size. The world of colloids exists between this size and the size of individual molecules, down to about 10 Å. Consider one phase dispersed as particles in another phase, thus forming a continuous medium. With successively smaller and smaller particles within this size range, eventually a limit will be reached at which the two phases become one. An example of such a single phase is a micellar solution, which consists of amphiphilic molecules associated into an aggregate. It is a colloidal solution, and we call it an association colloid. The individual molecules, however, form a molecular solution. In this small size range of colloids we can also find various macromolecules, such as proteins, in solution.

If wheat flour is stirred in an excess of water, the proteins will cover the entire range of sizes of colloidal dispersions. Some of these proteins are insoluble in water but can still be dispersed. The dispersed particles, however, tend to collect into aggregates, and larger aggregates will form a sediment together with starch when the stirring ceases. The stable water solution will therefore contain only small particles—monomers of the water-soluble fraction of proteins. An important feature characterizing colloidal dispersions is the size of the interface between the particles and the continuous phase, the total surface area of the particles. The fat globule in milk, for example, exposes an interface between fat and water of almost 10 m^2 per gram of milk. It is obvious that the nature of this interface plays a central role in our understanding of numerous properties of milk products, such as the separation of cream, the whipping of cream, and the formation of butter by phase inversion.

The importance of surface structure for colloidal phenomena is the reason for the close relation between surface science and colloidal science. This chapter presents the fundamental aspects, on the colloidal level, of the changes of the wheat endosperm from milling via dough mixing, fermentation, and heating to the final bread. Various crucial factors involved in baking properties—for example, the formation of gas cells and the gas-holding capacity of the dough—become obvious once we understand the underlying laws of surface and colloid science.

II. INTERFACES—SURFACE ENERGY AND SURFACE TENSION

Molecules in a liquid or in the bulk of a solid have neighbors in all three dimensions to interact with. In the surface layer, however, the molecules can interact only downwards toward the bulk or laterally within the surface plane. This is the reason for the existence of a *surface free energy*, which is the energy needed to increase the surface (or to bring molecules from the bulk to the surface layer). The surface free energy of a pure water surface toward air is about 73 mJ/m^2, whereas it is much lower for nonpolar liquids such as triglyceride oil (about 30 mJ/m^2). The surface energy is determined experimentally via the *surface tension* (γ), which is the force in millinewtons per unit length in meters that acts against increasing the area.

A drop hanging at the edge of a tube remains there because of surface tension (the mass of the drop is balanced by the surface tension), and this phenomenon provides one method to determine surface tension. Another method, described in the next section, is used to study the effect of surface-active molecules on the surface free energy. A third method is to use a capillary, provided that the walls are completely wetted by the liquid. The capillary force that causes the liquid to rise through the capillary tube is due to surface tension balancing the mass of liquid in the capillary above the level of the liquid outside the capillary.

III. SURFACE-ACTIVE MOLECULES—SELF-ASSEMBLY IN WATER AND MONOMOLECULAR SURFACE FILMS

In living tissues two groups of molecules tend to accumulate at interfaces: lipids and proteins. They are therefore classified as *surface-active molecules*, or *amphiphiles*. The driving force is their ability to reduce the surface energy between water and a gas phase or the interfacial energy between oil and water (or between solids and oil or water). Surface-active simple molecules such as lipids have one hydrophilic region; the rest of the molecule is hydrophobic. At an oil/water interface, the molecules of a monomolecular amphiphilic film will be oriented with their hydrophilic (water-attracting) region toward the water and their hydrophobic (water-repelling) region toward the oil.

Amphiphilic molecules form organized structures in bulk water by self-assembly. They do so because of hydrophobic effect, which is a tendency of the hydrocarbon region of the molecule to avoid water contact as it breaks the hydrogen bonds between water molecules. The structures obtained by such self-assembly of lipid molecules in water are further described below.

Suppose we have a pure water surface in a trough as shown in Fig. 1 with barriers defining the area. If a surface-active substance, for example, a long-chain fatty acid is spread from a solvent between the barriers, it is possible to record the pressure (π) versus molecular area of the fatty acid (A). The π–A isotherm is known from extensive studies of "insoluble" lipid monolayers to reflect the structure of the monomolecular film, as illustrated in Fig. 2. There are, in fact, the same structures as in the crystalline state of the lipid (solid state of the monolayer), in the lamellar liquid crystalline state (liquid condensed monolayer), or in the gaseous state. These corresponding lipid structures are described in later sections.

The surface film pressure π acts against the surface tension. Thus the surface film pressure is identical to the reduction in surface tension:

$$\pi = \Delta\gamma \tag{1}$$

Any protein in an aqueous solution will tend to go to the surface toward air, and the conformation and orientation it adopts will reduce the interfacial energy. A typical value of the reduction in interfacial tension when an excess of protein is present is about 20 mN/m. The absorption of proteins is usually irreversible, contrary to the behavior of lipids. This is due mainly to the size of the molecule. The protein molecule is often unfolded, and many water-insoluble segments of the peptide chain will be above the water surface. To undergo desorption, these segments would have to detach from the surface at the same time, which is very unlikely.

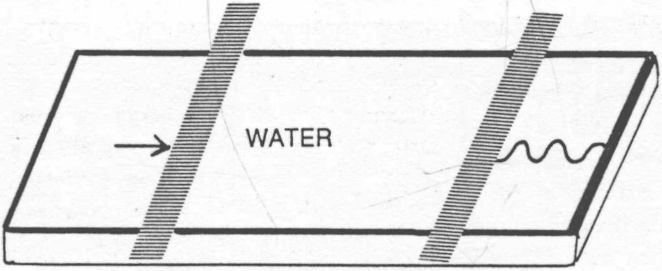


Fig. 1 Surface balance. One barrier can be moved to vary the area, whereas the other can record the presence of the surface film by the spreading pressure of the monolayer.

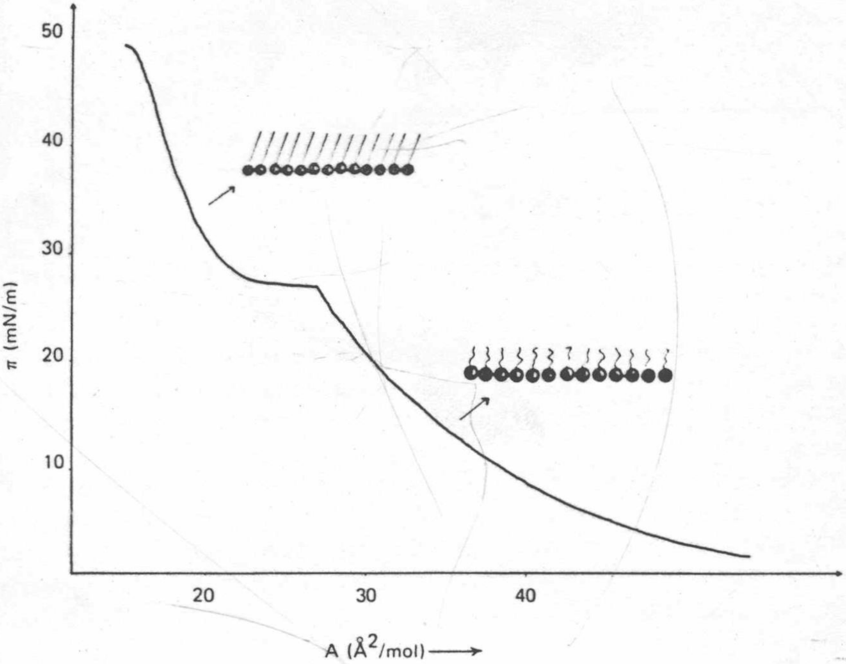


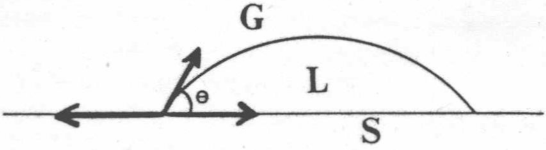
Fig. 2 Monolayer phases of a simple amphiphilic substance, one with lipid chains and the other (at high pressure) with crystalline chains. Polar heads of the molecules are indicated by circles, and the hydrocarbon chains by their axes.

Surface tension can be studied under various conditions using the surface balance, and even complex systems such as wheat lipids and wheat proteins can be successfully analyzed by spreading the corresponding monolayers, as will be described.

IV. INTERFACES OF SOLIDS—CRITICAL SURFACE TENSION OF WETTING

The surface energy of solids cannot be determined easily. A lot can be learned, however, from wetting properties. If a drop of liquid is put on the surface of a solid, it can either spread spontaneously, exhibiting complete wetting, or form a certain contact angle (θ) as shown in Fig. 3. The equilibrium conditions are given by the equation relating the interfacial tensions between the liquid and solid, between solid and gas, and between gas and liquid.

By studying the wetting properties using different polar/nonpolar liquids, it is possible to get indirect information on the surface properties of solids. A



$$\gamma_{GS} = \gamma_{GL} \cos\theta + \gamma_{LS}$$

Fig. 3 Interfacial tensions (γ) determining the contact angle (θ) of a droplet on a solid.

particularly useful concept is the critical surface tension of wetting, which is derived by plotting the cosine of the contact angle versus surface tension as shown in Fig. 4. The extrapolation to wetting gives the critical surface tension of wetting (γc).

Solid surfaces can be classified as low-energy surfaces (e.g., polyethylene, which has a surface energy $\pi \approx 30$ mJ/m^2) or high-energy surfaces. Pure metals have values of a few thousand millijoules per square meter in surface free energy, whereas the values for metal oxides are considerably lower. A liquid with a certain surface tension will always spread and wet a surface with a higher surface free energy.

V. THE ELECTRIC DOUBLE LAYER

When particles contain charged groups or have an adsorbed monolayer of an ionic surface-active substance that forms an interface toward water, there will also be an adsorbed layer of counterions close to the surface. The nature of this electric double layer is of utmost importance to an understanding of the stability of colloidal dispersions in water. The distribution of charges as reflected by the surface potential is illustrated in Fig. 5.

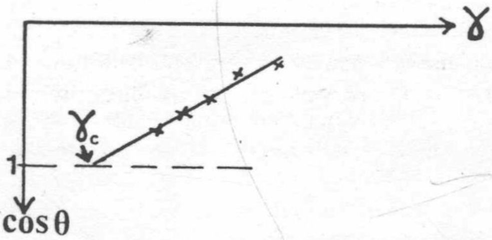


Fig. 4 Critical surface tension (γc) of wetting. Different liquids are used, and their contact angles (θ) recorded. The plot of cos θ versus surface tension gives the critical surface tension of wetting by extrapolation to contact angle 0°.

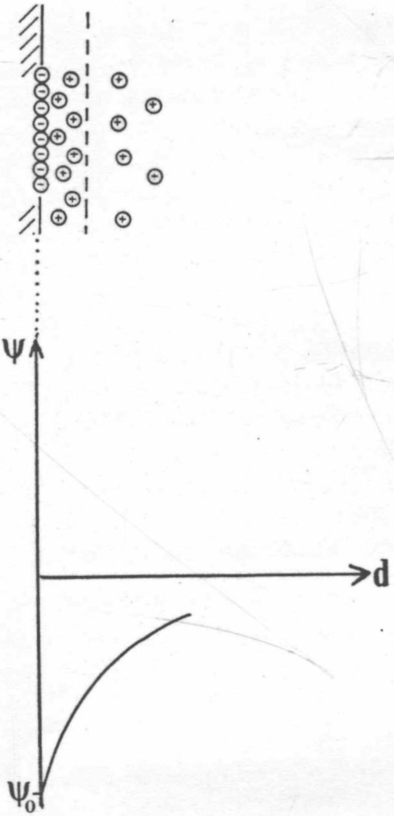


Fig. 5 Electric double layers as illustrated, of ionic distribution outside a surface, exposing negative groups.

The surface potential (ψ) has an exponential falloff

$$\psi = \psi\, e^{-\kappa d} \tag{2}$$

where d is distance from the surface and κ is directly proportional to the charge of the counterion and the square root of the concentration of the electrolyte in water. Thus added salt will compress the double layer. The repulsive force from this electric double layer is the basis for colloidal stability, as shown below.

A. The DLVO Theory

Deryaguin and Landau in the Soviet Union and Verwey and Overbeck in The Netherlands presented a simple theory more than half a century ago on the forces stabilizing colloidal dispersions. This theory, known as the DLVO theory, is still most useful. It describes the interaction energy between equal particles as a sum