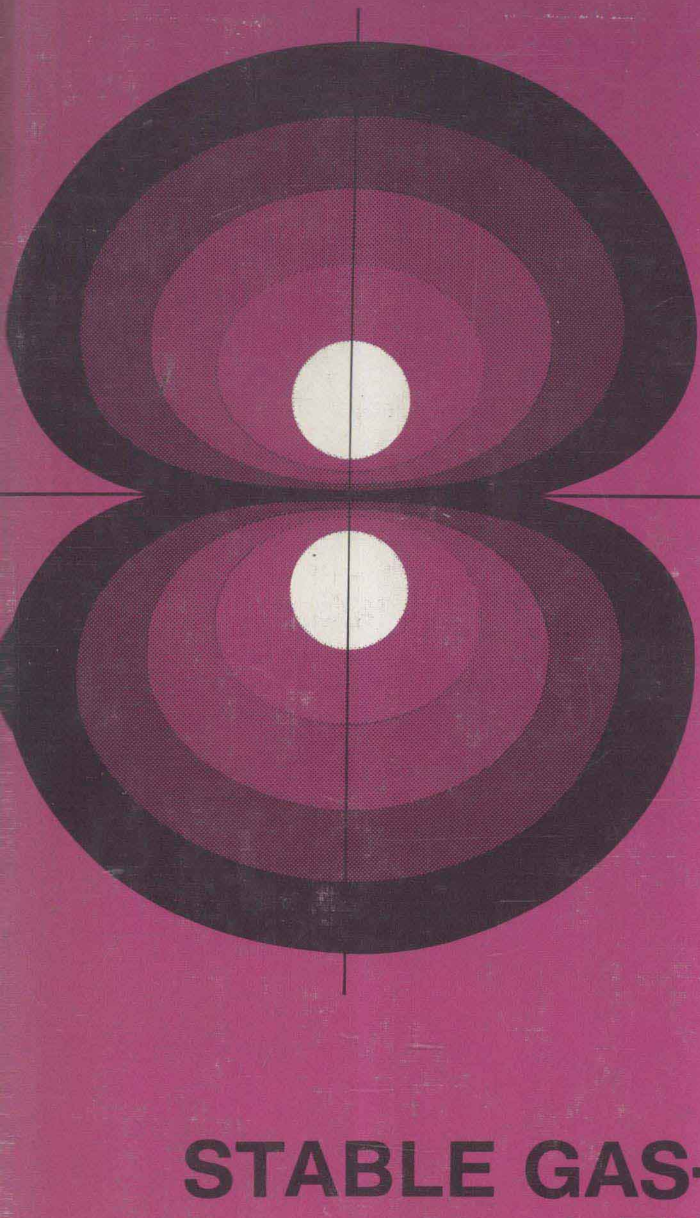
studies in physical and theoretical chemistry



40

STABLE GAS-IN-LIQUID EMULSIONS

Production in Natural Waters and Artificial Media

Joseph S. D'Arrigo

elsevier

studies in physical and theoretical chemistry 40

STABLE GAS-IN-LIQUID EMULSIONS

Production in Natural Waters and Artificial Media

JOSEPH S. D'ARRIGO

CAVitation-CONtrol Technology,
23A Brickyard Road, Farmington, CT 06032, U.S.A.

ELSEVIER
Amsterdam — Oxford — New York — Tokyo 1986

ELSEVIER SCIENCE PUBLISHERS B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Distributors for the United States and Canada:

ELSEVIER SCIENCE PUBLISHING COMPANY INC.
52, Vanderbilt Avenue
New York, N.Y. 10017, U.S.A.

Library of Congress Cataloging-in-Publication Data

D'Arrigo, Joseph S.
Stable gas-in-liquid emulsions.

(Studies in physical and theoretical chemistry ; 40)
Bibliography: p.
Includes index.
1. Emulsions. 2. Liquids. 3. Bubbles. I. Title.
II. Series: Studies in physical and theoretical
chemistry ; v. 40.
TP156.E6D37 1985 660.2'94514 85-27372
ISBN 0-444-42566-7 (U.S.)

ISBN 0-444-42566-7 (Vol. 40)
ISBN 0-444-41699-4 (Series)

Printed in The Netherlands

studies in physical and theoretical chemistry 40

STABLE GAS-IN-LIQUID EMULSIONS

Production in Natural Waters and Artificial Media

studies in physical and theoretical chemistry

Other titles in this series

1 R. Ginell, Association Theory
2 T. Boublik, I. Nezbeda and K. Hlavatý, Statistical Thermodynamics of Simple Liquids and Their Mixtures
3 P. Hobza and R. Zahradnik, Weak Intermolecular Interactions in Chemistry and Biology
4 S. Fraga, K.M.S. Saxena and M. Torres, Biomolecular Information Theory
5 A. Vértes, L. Korecz and K. Burger, Mössbauer Spectroscopy
6 H.E. Edwards, S. Navaratnam, B.J. Parsons and G.O. Phillips (Editors), Radiation Biology abd Chemistry: Research Developments
7 D.C. Walker (Editor), Origins of Optical Activity in Nature
8 F.J. Comes, A. Müller and W.J. Orville-Thomas (Editors), Spectroscopy in Chemistry and Physics, Modern Trends
9 A. Chełkowski, Dielectric Physics
10 A.G. Walton (Editor), Structure and Properties of Amorphous Polymers
11 S. Traśatti (Editor), Electrodes of Conductive Metallic Oxides
12 B.E. Conway, Ionic Hydration in Chemistry and Biophysics
13 I. Hargitta and W.J. Orville-Thomas (Editors), Diffraction Studies
14 G. Földiák, Radiation Chemistry of Hydrocarbons
15 D.A.J. Rand, G.P. Power and I.M. Ritchie (Editors), Progress in Electrochemistry
16 Z. Hippe (Editor), Data Pocessing in Chemistry
17 D. Papoušek and M.R. Aliev, Molecular Vibrational-Rotational Spectra
18 G. Náray-Szabó (Editor), Steric Effects in Biomolecules
19 R. Paul, Field Theoretical Methods in Chemical Physics
20 W.B. Person and G. Zerbi (Editors), Vibrational Intensities in Infrared and Raman Spectroscopy
21 R. Carbó (Editor), Current Aspects of Quantum Chemistry 1981
22 Yu.N. Molin (Editor), Spin Polarization and Magnetic Effects in Radical Reactions
23 J. Maruani and J. Serre (Editors), Symmetries and Properties of Non-Rigid Molecules
24 G. Spach (Editor), Physical Chemistry of Transmembrane Ion Motions
25 B.V. Thosar and P.K. Iyengar (Editors), Mössbauer Spectroscopy: Applications to Physics, Chemistry and Biology
26 E. Wyn-Jones and J. Gormally (Editors), Aggregation Processes in Solution
27 N. Tanaka, H. Ohtaki and R. Tamamushi (Editors), Ions and Molecules in Solution
28 R.B. King (Editor), Chemical Applications of Topology and Graph Theory
29 W.N. Hansen, D.M. Kolb and D.W. Lynch (Editors), Electronic and Molecular Structure of Electrode — Electrolyte Interfaces
30 D. Shaw, Fourier Transform NMR Spectroscopy (second revised edition)
31 T. Matsuura (Editor), Hot Atom Chemistry
32 P. Lacombe (Editor), Physical Chemistry of the Solid State: Applications to Metals and their Compounds
33 A.B.P. Lever, Inorganic Electronic Spectroscopy (second edition)
34 D.A.J. Rand and A.M. Bond (Editors), Electrochemistry: the Interfacing Science
35 F. Lahmani (Editor), Photophysics and Photochemistry above 6 eV
36 C. Nagata, M. Hatano, J. Tanaka and H. Suzuki (Editors), Biomolecules: Electronic Aspects
37 W.J. Orville-Thomas, H. Ratajczak and C.N.R. Rao (Editors), Topics in Molecular Interactions
38 R.R. Dogonadze, E. Kálmán, A.A. Kornyshev and J. Ulstrup (Editors), The Chemical Physics of Solvation. Part A. Theory of Solvation
39 G. Földiák (Editor), Industrial Application of Radioisotopes

To
Sachie and Paul

PREFACE

The occurrence of dilute gas-in-liquid emulsions in natural waters has been and continues to be a topic of great importance to workers in many fields of fundamental and engineering sciences. Specifically, the existence of long-lived gas microbubbles in fresh water, sea water, and other aqueous liquids including physiological fluids has been postulated and/or demonstrated by numerous investigators over the last three decades. In spite of this, no comprehensive account of the predominant physicochemical/biochemical mechanism by which such gas microbubbles (0.5-100 μm in diameter) are stabilized exists in the literature, and this book is intended to fill that gap. It begins with a review of the evidence for surfactant stabilization of the natural microbubbles commonly occurring in fresh water and sea water. The discussion continues with a description of microbubble experiments employing aqueous gels and soil extracts, then identifies many of the characteristic biochemical components of natural microbubble surfactant, and goes on to describe various geochemical, surface, and structural properties of the natural surfactant mixture. Combined with findings from physiological studies, this information is utilized for the successful production of relatively concentrated, significantly stable (hours to days), gas-in-liquid emulsions in artificial media, as described in the final chapters of the book.

A detailed knowledge of the predominant physicochemical/biochemical mechanism by which gas microbubbles are stabilized in aqueous media is of practical importance to numerous and varied fields: acoustic and hydrodynamic cavitation, commercial oil recovery, hydraulic and ocean engineering, waste-water treatment, chemical oceanography, meteorology, marine biology, food technology, echocardiography, and the continual medical problem of decompression sickness. Many of these applications derive from the fact that persisting microbubbles affect the acoustical and mechanical characteristics of water, increasing attenuation, scattering ultrasonic energy, changing speed of propagation, and grossly reducing the tensile strength. Accordingly, the artificial enhancement of tensile strength in particular, i.e., through low-cost chemical destruction of the surfactant-stabilized microbubbles in water, is a desirable goal in order to improve the performance of devices normally limited in maximum output by cavitation, such as ship sonar, pumps, turbines, and propellers. The potential gains, such as the prevention of cavitation damage, obtaining a greater output from a given size or weight of equipment, i.e., an increase in return for a given economic investment, are all quite tempting. Separate, more fundamental considerations include the fact that microbubble populations, well known by marine biologists to exist in the upper ocean, can become attached to particles within the water column; this attachment affects the settling rates of marine detritus and, hence, has an impact on the ocean food chain. Also, bursting of bubble populations at the sea surface, with the concomitant production of a sea-salt aerosol and the ejection of organic material into the atmosphere, is of special interest to meteorologists, oceanographers, and environment specialists. As concerns industry, although adsorptive bubble separation has been used commercially for more than half a century (principally in froth flotation to separate minerals from ores), the related process of microflotation (requiring much smaller bubble sizes) was developed more recently for efficiently removing various colloidal pollutants from water and shows promise as a viable procedure for the treatment of water and waste waters. The process utilizes frothing agents, a potential area for further development, to promote the formation of microbubbles and these amphiphilic substances may contribute to the maintenance of a stable foam. Of more general interest to industry is the related, wider area of two-phase bubbly flows. Besides fundamental engineering interest, which aims at a deeper understanding of interphase momentum, heat, and mass transfer, there is a strong demand for practical information to optimize those systems in which two-phase flows occur, e.g., a motive liquid and an entrained gas. One common example of this type of chemical engineering operation, which might well be improved by the production of surfactant-stabilized gas-in-liquid emulsions, is the entrainment and pumping of corrosive fumes that are otherwise difficult to deal with. Moreover, artificially produced, surfactant-stabilized microbubbles would also have specific medical applications; for example, there is the immediate potential for developing longerlasting and more uniform contrast agents for echocardiography, where injected air microbubbles have already been shown to travel with intracardiac velocities similar to those of red blood cells. Apart from echocardiography, another very promising clinical application of these nontoxic, synthetic microbubbles would be the ultrasonic monitoring of local blood flow in the abdomen (analogous to the current use of ordinary microbubbles to monitor myocardial perfusion). Such refined ultrasonic blood flow measurements, utilizing locally injected synthetic microbubbles, have the potential for providing better clinical detection of tumor neovascularization as well as any subtle changes in the normal vascularization patterns of organs neighboring abdominal masses. Hence, through the use of synthetic microbubbles, ultrasound may now provide much earlier diagnosis of abdominal masses; this early detection may well improve treatment of several classes of serious abdominal cancers, a notorious example being pancreatic cancer.

The underlying chemical principles covered in the chapters are presented in sufficient detail for this book to be useful to all interested readers with a working knowledge of chemistry, physics, and biology. Accordingly, the level of readership is intended to include graduate students, researchers, and professional people from widely varying fields. Furthermore, due to the many above-mentioned current and potential applications of stable gas-in-liquid emulsions, the appropriate readership of this book is likely to be found in industry, universities, and government laboratories alike.

Thanks are due to the following colleagues for their collaboration on some of the original investigations described in this book and/or their generous help with various experimental measurements: William Barker, J. Howard Bradbury, Kai-Fei Chang, Stephanie A. Ching, John F. Dunne, Richard J. Guillory, Brendon C. Hammer, Jacob N. Israelachvili, Kathleen M. Nellis, Barry W. Ninham, Noboru Oishi, Richard M. Pashley, Neil S. Reimer, P. Scott Rice, Cesareo Saiz-Jimenez, Kent Smith, Ourai Sutiwatananiti, and Linda Vaught. Finally other acknowledgments, in addition to those appearing in the chapters, include permission to use quoted material appearing on: p. 13, Copyright 1981 by the AAAS; p. 24, Copyright 1972 by the ASME; and pp. 7, 10, 16, and 93-94, Copyright 1975, 1978, 1978, and 1974, respectively, by the Pergamon Press, Ltd.

Joseph S. D'Arrigo

CONTENTS

Chapter 1

OCCURRENCE OF DILUTE GAS-IN-LIQUID EMULSIONS IN NATURAL WATERS

Dilute gas-in-liquid emulsions, namely, significantly stable (hours to days) suspensions of long-lived air microbubbles, in natural waters is a topic of great concern to workers in many fields of fundamental and engineering sciences. Specifically, the existence of stable gas microcavities or microbubbles in fresh water (ref. 1-29), sea water (ref. 5,15-17,27,30-33), and other aqueous liquids including physiological fluids (ref. 2, 29,34,35) has been postulated and/or demonstrated by numerous investigators over the last few decades. However, there is far less agreement in the literature as to the predominant physicochemical/biochemical mechanism by which such gas microbubbles, 0.5∼100 μm in diameter, are stabilized. A detailed knowledge of this physicochemical/biochemical stabilization mechanism in aqueous media is of practical importance to numerous and varied fields: hydrodynamic (ref. 6,23,27) and acoustic (ref. 7,9-19, 21,28) cavitation, hydraulic and ocean engineering (ref. 15-17, 27), waste-water treatment (ref. 36), commercial oil recovery (ref. 37), chemical oceanography (ref. 38-42), meteorology (ref. 43-48), marine biology (ref. 49,50), food technology (ref. 51-53), echocardiography and the continual medical problem of decompression sickness (ref. 49,54-56). Several of these applications are described individually below.

1.1 PRACTICAL IMPORTANCE OF STABLE MICROBUBBLES

1.1.1 Hydrodynamic cavitation, hydraulic and ocean engineering

As Acosta and Parkin emphasize in a past review of this topic (ref. 27), hydrodynamicists do not need to be reminded that cavitation inception, with the pervasive role it occupies in naval architectural hydrodynamics, remains as a basic problem plaguing the worker in the laboratory and field alike. One of the more confusing aspects of this phenomenon has been its lack of repeatability between experiments carried out on similar test bodies in different test facilities (ref. 27) or even on different types of bodies in the same test facility (ref. 16,27).

For instance, appreciable tensile strength has occasionally been noted in water tunnels (ref. 16). (The tensile strength of a liquid is defined here as the minimum tensile stress in the liquid at which it ruptures or cavitates (ref. 57).) The inception of cavitation in these water tunnels has occurred at higher stress levels than ordinarily expected. Higher flow velocities or lower tunnel pressures than normal have been needed to produce cavitation about a test body. The tensile strength acts as if an additional static head were present in the system. In this case, appreciable tensile strength is undesirable in order to make for a uniformity of test results, and duplicate "prototype" conditions (ref. 16).

Alternately, the enhancement of tensile strength is a desirable goal in order to improve the performance of hydraulic devices normally limited in maximum output by cavitation, such as pumps, turbines, and propellers. The potential gains, such as the prevention of cavitation damage, obtaining a greater output from a given size or weight of equipment, i.e., an increase in return for a given economic investment, are all quite tempting (ref. 16).

The detailed work of Bernd (ref. 15-17) and other investigators has shown that the tensile strength of water is set by the gas nuclei (i.e., microbubbles) present in the water. (Accordingly, the earlier-mentioned definition of the tensile strength of a liquid can be restated as the minimum tensile stress at which the gas nuclei in the liquid start to "explode". This property is also often referred to as the "cavitation susceptibility" (ref. 57).) Using specially constructed sonar transducers, the behavior of gas nuclei was followed by Bernd by measuring tensile strength. Surface films were found to form around the gas nuclei, retarding the acquisition of tensile strength by the water. To obtain a better understanding of these surface films, various waters were tested. Also surface films were created about gas nuclei (i.e., microbubbles) from solutions of hydrocarbons (i.e., acyl lipids) and proteins in water (ref. 16).

Hence, in practical flow situations the water is not pure; gas bubbles and small impurities are embedded within the liquid. Small gas bubbles can stay in suspension for a long time, because the relative motion in an upward direction due to gravity is opposed by transport in the downwards direction by turbulent diffusion (ref. 57). These microbubbles are initially trapped