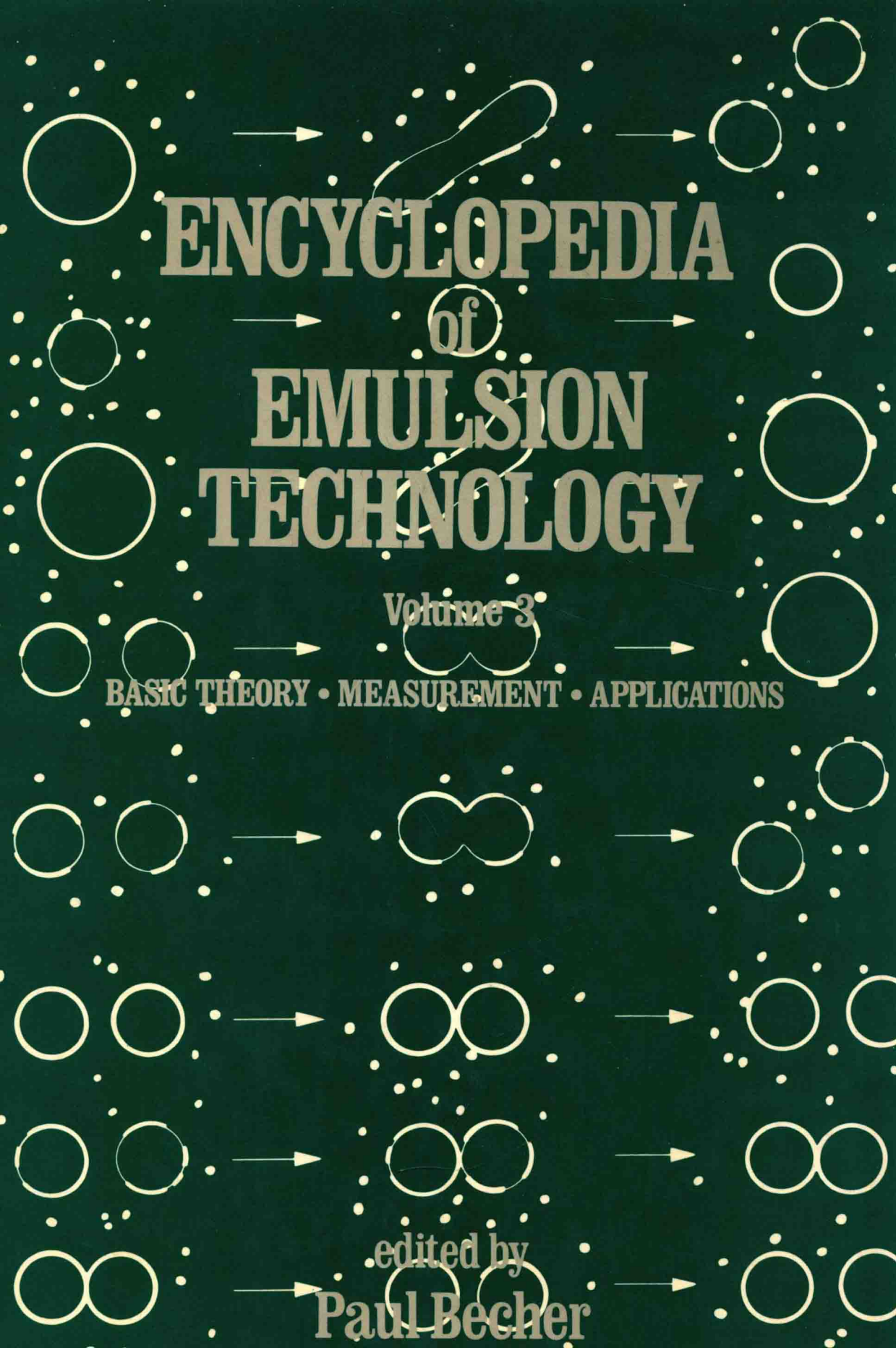

ENCYCLOPEDIA of EMULSION TECHNOLOGY

Volume 3

BASIC THEORY • MEASUREMENT • APPLICATIONS

edited by
Paul Becher

ENCYCLOPEDIA OF EMULSION TECHNOLOGY

VOLUME 3

Basic Theory
Measurement
Applications

Edited by PAUL BECHER
Paul Becher Associates Ltd.
Wilmington, Delaware

MARCEL DEKKER, INC. NEW YORK and BASEL

Library of Congress Cataloging-in-Publication Data

(Revised for volume 3)

Encyclopedia of emulsion technology.

Includes bibliographical references and indexes.
Contents: v. 1. Basic theory -- v. 2. Applications--
v. 3. Basic theory, measurement, applications.
1. Emulsions. I. Becher, Paul.
TP156.E6E62 1983 660.2'94514 82-18257
ISBN 0-8247-1876-3 (v. 1)
ISBN 0-8247-1877-1 (v. 2)
ISBN 0-8247-1878-X (v. 3)

COPYRIGHT © 1988 by MARCEL DEKKER, INC. ALL RIGHTS RESERVED

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

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

ENCYCLOPEDIA OF EMULSION TECHNOLOGY

VOLUME 3

Basic Theory
Measurement
Applications

Preface

This is the third volume of the *Encyclopedia of Emulsion Technology*. In previous volumes we have reviewed the pertinent basic theory (Volume 1) and applications of emulsion systems (Volume 2). Although in the present volume we introduce a new topic—measurements on emulsions—we are also doing a little housekeeping by including two additional chapters on basic theory and another two on applications.

The first chapter in the basic theory section, by David H. Melik and H. Scott Fogler, deals with the important problem of sedimentation in disperse systems (which exhibits itself as "creaming" in emulsions), and the use of this phenomenon to establish the stability of the system. From this point of view, this chapter might equally well have been included in the section on measurements.

The second chapter in the basic theory section, by Jean-Louis Salager, is an important contribution to our understanding of the phenomenon of emulsion inversion. When, some ten years ago, I first came upon catastrophe theory it immediately occurred to me that this could be an elegant way of treating inversion. It has remained, however, for Prof. Salager to demonstrate this.

Turning to the field of measurements, in the first chapter in this section, Clyde Orr treats what may be possibly the most important measurement one can make on an emulsion, namely, the particle size distribution. Following this, Heinz Hoffmann and Herbert Thurn describe the difficult technique of neutron scattering, which gives much useful information about the structure of emulsions, in particular, microemulsions. Unfortunately, the experimental technique is such that the method is not widely available; on the other hand, knowledge of the technique is important, and that is what the authors wish to convey.

The two remaining chapters in this section deal with methods of representing emulsion data. Although triangular diagrams are widely used, especially for microemulsions, a surprising number of chemists and

此为试读,需要完整PDF请访问: www.ertongbook.com

engineers aren't really clear as to how they *work*. Indeed, there are not a few diagrams in the literature which are thermodynamically impossible—but that's another matter! Raymond Mackay has contributed a chapter on triangular diagrams which develops the theory of such figures, and gives useful examples of their application. Finally, Kenneth J. Lissant describes the technique of using glyphs to represent a large amount of data in an extremely compact way.

Turning to the final section, "Applications," Howard Bampfield and John Cooper describe an extremely important, and, in my opinion, too little known, application of emulsion systems. Emulsion explosives are convenient to use and remarkably safe. However, the formulation of such an emulsion, combining explosive power with stability, is a theoretical and practical problem of considerable difficulty.

Finally, Bruce Davis discusses the use of emulsion systems in the petroleum industry. In the winning of petroleum, numerous emulsion types arise naturally, or are produced deliberately. Davis reviews the theoretical basis for these emulsions and, in addition, enhances our knowledge of the theoretical basis of HLB.

We regret that the chapter on surfactant properties previously announced for this volume could not be undertaken. Prof. Salager's chapter, written on extremely short notice, was happily available to fill the gap.

I cannot conclude without noting that my dear wife, Jane, has continued to be my support and consistent help in producing these volumes. The first volume was formally dedicated to her, but, by extension, so are all the volumes in this work.

Paul Becher

Contributors

HOWARD ANTHONY BAMPFIELD *
Explosives Research Laboratory, C-I-L Inc., McMasterville, Quebec, Canada

PAUL BECHER
Paul Becher Associates Ltd., Wilmington, Delaware

JOHN COOPER †
Detonation Research Group, ICI PLC, Stevenston, Ayrshire, Scotland

BRUCE W. DAVIS
Production Research Department, Chevron Oil Field Research Company, La Habra, California

H. SCOTT FOGLER
Department of Chemical Engineering, The University of Michigan, Ann Arbor, Michigan

HEINZ HOFFMANN
Department of Physical Chemistry, University of Bayreuth, Bayreuth, West Germany

KENNETH J. LISSANT ‡
Petrolite Corporation, St. Louis, Missouri

RAYMOND A. MACKAY
Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, Maryland

DAVID H. MELIK §
Department of Chemical Engineering, The University of Michigan, Ann Arbor, Michigan

CLYDE ORR
Micromeritics Instrument Corporation, Norcross, Georgia

Current affiliations:
*ICI Group Technical Centre, ICI, McMasterville, Quebec, Canada
†Group Explosives Technical Centre, ICI PLC, Stevenston, Ayrshire, Scotland
‡Consultant, Clever, Missouri
§Miami Valley Laboratories, The Proctor & Gamble Company, Cincinnati, Ohio

JEAN-LOUIS SALAGER
Laboratory FIRP, Universidad de los Andes, Mérida, Venezuela

HERBERT THURN, Ph.D.
Department of Physical Chemistry, University of Bayreuth, Bayreuth, West Germany

Contents of Volume 1: Basic Theory

Preface

Contributors

Introduction

1. Liquid/Liquid Interfaces
   Tharwat F. Tadros and Brian Vincent

2. Formation of Emulsions
   Pieter Walstra

3. Emulsion Stability
   Tharwat F. Tadros and Brian Vincent

4. Microemulsions
   Stig E. Friberg and Raymond L. Venable

5. Phase Properties of Emulsions: PIT and HLB
   Kōzō Shinoda and Hironobu Kunieda

6. Emulsion Droplet Size Data
   Clyde Orr

7. Rheological Properties of Emulsions
   Philip Sherman

8. Optical Properties of Emulsions
   Raymond S. Farinato and Robert L. Rowell

9. Dielectric Properties of Emulsions and Related Systems
   Marc Clausse

Index

Contents of Volume 2: Applications

Preface

Contributors

1. Demulsification
   Venugopal B. Menon and Darsh T. Wasan

2. Research Techniques Utilizing Emulsions
   Danièle Clausse

3. Medical and Pharmaceutical Applications of Emulsions
   Stanley S. Davis, Jonathan Hadgraft, and Karen J. Palin

4. Applications in Agriculture
   David Z. Becher

5. Applications in the Food Industry: I
   Niels J. Krog, Tom H. Riisom, and Kåre Larsson

6. Applications in the Food Industry: II
   Edgar N. Jaynes

7. Cosmetic Emulsions
   Miklos M. Breuer

8. Hydrophile-Lipophile Balance: An Updated Bibliography
   Paul Becher

Index

Contents

Preface iii

Contributors vii

Contents of Volume 1: Basic Theory ix

Contents of Volume 2: Applications xi

I BASIC THEORY

1. Fundamentals of Colloidal Stability in Quiescent Media 3
David H. Melik and H. Scott Fogler

2. Phase Transformation and Emulsion Inversion on the Basis of Catastrophe Theory 79
Jean-Louis Salager

II MEASUREMENT OF PROPERTIES

3. Determination of Particle Size 137
Clyde Orr

4. Emulsion Structure by Neutron Scattering 171
Heinz Hoffmann and Herbert Thurn

5. Use of Triangular Diagrams in the Study of Emulsions 223
Raymond A. Mackay

6. Use of Glyphs to Organize Data in Multivariant Systems 239
Kenneth J. Lissant

III APPLICATIONS

7. Emulsion Explosives 281
Howard Anthony Bampfield and John Cooper

此为试读,需要完整PDF请访问: www.ertongbook.com

8. Applications in the Petroleum Industry 307
Bruce W. Davis

IV APPENDIX 397
HLB: A Further Update
Paul Becher

Index 433

I
BASIC THEORY

1
Fundamentals of Colloidal Stability in Quiescent Media

DAVID H. MELIK* and H. SCOTT FOGLER / Department of Chemical Engineering, The University of Michigan, Ann Arbor, Michigan

I. Introduction 3

II. Population Balance Equation 8

III. Interparticle Forces: DLVO Theory 9

A. Features of the DLVO Theory 13
B. Non-DLVO Interparticle Effects 17

IV. Convective-Diffusion Equation 17

A. Flocculation Kinetics 22
B. Particle Creaming 37

V. Colloidal Stability: Simultaneous Flocculation and Creaming 39

A. Solution of the Population Balance Equation 39
B. Features of Simultaneous Flocculation and Creaming 41

VI. Delineation of Different Particle Loss Mechanisms 44

A. Gravity-Induced Flocculation versus Brownian Flocculation 44
B. Gravity-Induced Flocculation versus Creaming 46
C. Domains of Dominant Particle Loss Mechanisms 48

VII. Experimental Procedures 51

A. Initial Rate Experiments 52
B. Measuring Changes in the Particle Size Distribution 64

VIII. Future Research Needs 68

Symbols 71

References 75

I. Introduction

Colloidal dispersions (including emulsions and suspensions) are frequently encountered in industry and the environment. Common examples include milk, paint, blood, and atmospheric smog. Even though these dispersions are chemically different, they exhibit similar properties owing to the very small size of the suspended particles. Sizes generally range between 0.1

*Current affiliation: Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio

Table 1. Components Necessary for Predicting Colloidal Stability

Forces
1. Interparticle:
a. London-van der Waals attractive
b. Electric double layer repulsive
2. Gravitational
3. Hydrodynamic
4. Brownian motion
Kinetics
1. Creaming
2. Brownian flocculation
3. Gravity-induced flocculation
Population balances
1. Predict changes in the particle size distribution and particle concentration
2. Test changes in system parameters

and 10.0 μm in diameter. As a result, colloidal particles do not rapidly settle out of the continuous phase and are not readily filtered.

Although colloidal particles are capable of remaining suspended indefinitely, emulsions and suspensions are thermodynamically unstable. This instability arises from the large interfacial area, and therefore large surface energy, associated with finely dispersed systems. Consequently, in order to reduce the total interfacial area, colloidal particles tend to either flocculate irreversibly or to accumulate at an interface. These phenomena distinguish colloids from micellar and polymer solutions, which are in many ways similar but are thermodynamically stable and reversibly flocculated.

Because of this inherent instability, an underlying goal of colloidal studies is to predict a priori the "stability" of a given or desired colloidal dispersion. As shown in Table 1, there are three components necessary for quantitatively predicting colloidal stability: (i) the forces that dictate the particle motions; (ii) the kinetics of the colloidal breaking processes; and (iii) the population balance equations.

Under certain conditions an emulsion or suspension may be unstable to the extent that it breaks within a matter of seconds (e.g., vinegar and oil), whereas in other systems the colloidal breaking process may be so kinetically limited that the particles remain suspended for very long periods of time (e.g., polystyrene latexes). Consequently, an obvious concern in colloidal systems is quantifying the characteristic time for colloidal breaking mechanisms. It turns out that this characteristic time is highly dependent on the many forces that affect the particle motions. In quiescent media, these forces include Brownian motion, van der Waals attractive and electrostatic repulsive interparticle forces, gravitational forces, and hydrodynamic interactions. Hydrodynamic interactions arise from the resistance of the fluid that has to be pushed from in between two approaching particles.

The overall effect of these forces on emulsions and suspensions is manifested in the form of three coupled particle loss mechanisms: creaming, Brownian flocculation, and sedimentation (gravity-induced) flocculation. These breakage mechanisms are depicted in Fig. 1. In creaming, particles either rise or sediment out of the system as a result of the density difference between the particles and the suspending medium. Encounters between particles occur because of random Brownian motion, frequently resulting in particle aggregation if the interparticle interactions are favorable. Gravity-induced flocculation arises from the differential creaming rates of large and small particles. The large particles sweep out the slower-moving small particles in their path, often resulting in particle aggregation if the interparticle interactions are favorable. In the case of emulsions, coalescence of the particles can occur after flocculation.

In order to analyze rigorously the behavior of these particle loss mechanisms on colloidal stability, one must determine the rate at which these mechanisms are occurring. This can be accomplished by solving the governing convective-diffusion equation which describes the distribution of particles around a central or reference sphere. Because of the difficulties generally associated with solving the complete problem in which all the forces acting on the particles are of the same order of magnitude, models applicable for different magnitudes of interparticle, gravitational, and diffusional effects have been developed. Depending on the particle sizes and the net gravitational force, five important regimes can be identified:

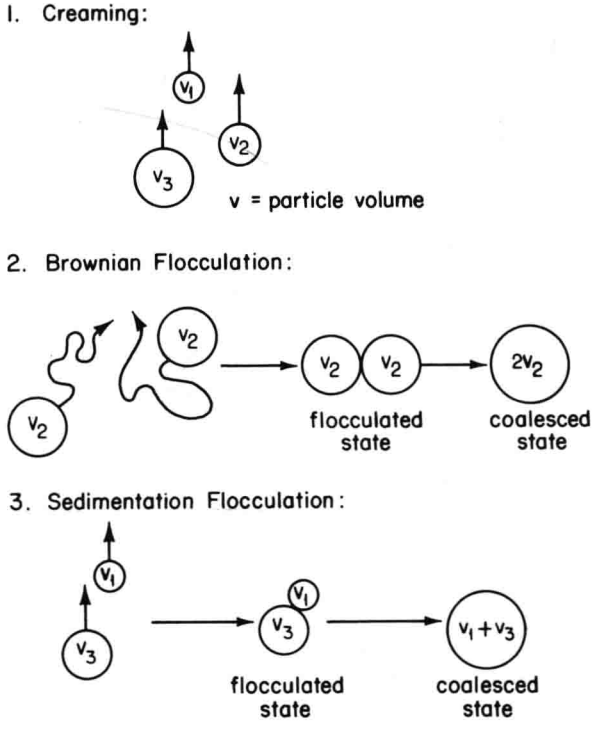

Figure 1. Colloidal breaking mechanisms in quiescent media.

此为试读,需要完整PDF请访问: www.ertongbook.com