Bubble and Foam Chemistry

This indispensable guide will equip you with a thorough understanding of the complete field of bubbles and foaming chemistry. Assuming only basic theoretical background knowledge, the book provides you with

- a straightforward introduction to the principles and properties of bubbles, foams and foaming surfactants underpinning the key ideas about why foaming occurs, how it can be avoided and how different degrees of antifoaming can be achieved;
- the latest test methods, including laboratory and industry-developed techniques;
- details on a range of differents kinds of foams, from wet detergents and food foams to polymeric, material and metal foams which connect theory with real-world applications and recent developments in foam research.

Combining academic and industrial viewpoints, this book is the definitive stand-alone resource for researchers, students and industrialists working on foam technology, colloidal systems in the field of chemical engineering, fluid mechanics, physical chemistry and applied physics.

Robert J. Pugh is a Visiting Professor at Nottingham Trent University. He is an active member of the foams community and has over 30 years experience in industry and university, having worked as a foam specialist for Dow Chemical and Unilever Research. He has also worked as a Professor at the Institute for Surface Chemistry, Stockholm, and at Luleå University, Sweden, and has acted as a consultant for Akzo Nobel, Nestlé, GlaxoSmithKline, Procter and Gamble, and Arizona Chemicals. Professor Pugh has co-authored and edited two previous books in the field of surface and colloid science and authored several highly cited review papers on the topic of foams and foaming.

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Preface

The aim of this book is to provide a comprehensive, well-structured insight into the physical chemistry of liquid foams which can be used by both academics and industrialists. Liquid foams may occur naturally or by design and may be desirable or undesirable. Generally, there is a multitude of complex causes of foaming and antifoaming and the text is structured to give clarity to the field by providing an up-to-date, state-of-the-art guide explaining the chemistry of real foam systems. It is hoped that the reader will achieve a reasonably clear understanding of why foaming occurs, how it can be measured and how it can be prevented. As the use of foams spans different disciplines, some introductory aspects of physics, chemical engineering and material science of foams are included but this is relatively easy to follow. This book is orientated toward the descriptive rather than the theoretical and contains many diagrams. It is also a rich source of information and references, arranged in a way which the reader should find useful and also provides an historical prospect to the area of foams and foaming.

The most popular academic books dealing solely with foams include the classics *Foams* by J. J. Bikerman (1973), published by Springer-Verlag, Berlin and *The Physics of Foams* by D. Weaire and S. Hutzler (1999), published by Clarendon Press, Oxford. Both of these books ran into several updated editions but considerable advancements in the field have been made since their publication. Other early texts are *Foams and Biliquid Foams-Aphrons* by F. Sebba (1987), published by Wiley and the two books – *Antifoaming* (edited by P. Garrett, 1993) and *Foams* (edited by R. K. Prud'homme and S. A. Kahn, 1996) – published in the *Surfactant Science Series* (Marcel Dekker). These are fairly well-read books but are essentially a collection of viewpoints which describe many varied aspects of foaming and antifoaming science. *Foam and Foam Films* by D. Exerowa and P. M. Kriglyako (1997), published by Elsevier in the *Studies in Interfacial Science Series*, has been well received but presents a strongly fundamental text with the main emphasis on thin films. More recently is the book *Foam Engineering*, edited by P. Stevenson (2012) and published by Wiley, covers rheology, flow and foam processing and is aimed toward the chemical engineering community. Another recent book, *Foams Structure and Dynamics* (2013) edited by a group of French scientists and published by Oxford University Press, was directed toward the Physics community.

There are many other books available but they are multi-authored, specialist texts edited by engineers, chemists, chemical engineers or physicists. They usually include an ad hoc assortment of specialist research or review papers focused on foams or foaming within specific areas. For example, an early book by Schraum (1994) covered the oil industry and E. Dickenson and coworkers edited several books on the food industry which included chapters on food foams. Another multi-authored book, *Foamspex*, came out as a European Union project and covers the large-scale applications and modeling of foam spreads and extinguishment aspects of firefighting foams. This was published by SP Sweden (the Swedish National Testing and Research and Fire Technology Institutes) in 2001. Other texts on polymer foam systems are more specialized, for example, *Polymer Foam Handbook*, edited by N. J. Mills and published by Elsevier (2007) and *Handbook of Polymeric Foams and Foam Technology*, edited by D. Klemper and coworkers and published by Hanser (2004).

This book is a single-authored, comprehensive text which gives a current and coherent picture of foam chemistry. The book will probably be of most interest to senior undergraduate and graduate students of physical chemistry, chemical engineering, surface and colloid chemistry, life sciences and applied physics. It is also aimed at scientists and engineers in industry who frequently encounter foams under practical conditions. In these cases, the presence, absence and nature of foam can determine the economic and technical success of the process. Although some prerequisite scientific knowledge is expected from the reader, only the bachelor's level in sciences is needed to adequately understand the principles presented. In fact, the book could prove to be of interest to less academic amateur scientists, for example, with interests in the brewing of beer.

The book contains twelve chapters. Chapter 1 outlines the most important properties of foams and their uses in everyday situations. The physical and chemical aspects of foams and foaming are reviewed and the main features of wet and dry foams are described. Surface active agents and the relevant basic thermodynamics are also introduced. Chapter 2 describes the nature and properties of chemical foaming surfactants together with their role in stabilizing bubbles. Chapter 3 is an important chapter from a fundamental viewpoint since it covers soap films, which are the basic structural elements in foams, and it reviews the role of the intermolecular forces which define the stability of thin films. Techniques for measurement of the stability and draining of foam films are also discussed. In Chapter 4, an overview of the different types of processes in foaming is presented. These include the ascent of bubbles in liquids, the drainage of liquids through foams and the diffusion of gas through the foam, humidity and evaporation. Chapter 5 covers the generation of foams and includes a range of methods used both in laboratory and in industry. In Chapter 6, the coalescence of bubbles and techniques for measuring the coalescence process are described. Coalescence of bubbles in solutions of different types of inorganic electrolytes is reviewed in light of recent experiments in which the bubble approach speed is taken into consideration. Chapter 7 discusses the classification of bubble and foam stability and the different types of stabilization mechanisms which can operate. In addition, the various types of additives which can be used in stabilization of foam systems are summarized.

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In Chapter 8, the historic background of particle stabilized foams is presented together with their use in established processes such as deinking and flotation. The role of contact angle, particle shape, charge, detachment forces, capillary pressure and the influence of the formation of different types of particle networks is discussed. Chapter 9 covers foaming in non-aqueous liquids, which is less commonly encountered in non-aqueous fluids than in water-based media, but it is an important topic to consider. It occurs in a wide range of industrial processes – for example, during the processing of crude oils, drilling fluids, lubricants, solvent (base cleaners), etc. Chapter 10 covers defoaming and antifoaming. Problems are caused by foaming throughout a range of industrial processes – for example, in the production and processing of paper, pharmaceuticals, materials, textiles, coatings, crude oils, washing, leather, paints, adhesives, lubrication, fuels, heat transfer fluids, etc. and in the processing of food and beverages such as sugar beet, orange and tomato juice, beer, wine and mashed potatoes. The different types of antifoaming additives used to prevent formation and destruction of foams are classified and also the physical chemical mechanisms involved. Foam test methods are described in Chapter 11, including both laboratory and industrially developed techniques. Finally, in Chapter 12, several new developments in the area of foam research are reviewed. This includes the growth and stability of foams in microgravity and mechanisms involved in the production of metal foams at high temperature, which have the potential to be used in the automobile and aircraft industries. In addition, foaming in the environment is documented (natural waters, sea waters and polluted waters). Insects, mammals and reptiles produce stable foams from bio-surfactants or surface active proteins which have complex structures.

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Symbols

A	surface area of foam or foam film
A_i	Initial area of foam film
A_s	cross-sectional area of foam film
A^f	area of liquid film
a	activity of solute
a_h	effective head group area of surfactant
a_c	condensation coefficient
B_c	film breaking coefficient
B, B_1, B_3, B_4	proportionality constants
C	concentration
C_s	surfactant concentration in solution
C_{el}	electrolyte concentration in solution
$C_{el,cr}$	critical electrolyte concentration
C_b	concentration of black spot formation
C_{NBF}	critical surfactant concentration for Newton black film formation
C_e	equilibrium surfactant concentration of Newton black film stability
C_{max}	maximum surfactant concentration (for bubble coalescence)
C_{PB}	transitional electrolyte concentration (Prince and Blanch)
D	diffusion coefficient of surfactant molecules in bulk solution
D_g	diffusion coefficient of gas from a shrinking bubble
D_f	diffusion coefficient of gas
D_{eff}	effective diffusion coefficient of gas
D_w	diffusion coefficient of gas through aqueous core of thin film
D_s	surface diffusion coefficient
D_v	coefficient of vacancy diffusion in an amphiphile bilayer
d	bubble diameter
d_{eq}	bubble equivalent diameter
d_v	bubble vertical diameter
d_h	bubble horizontal diameter
dx	small change in distance caused by stretching liquid film
E_g	Gibbs coefficient of surface elasticity
E_a	activation energy
E_c	entry coefficient
E_g	generalized entry coefficient

E^*	complex dilational visco-elastic modulus
E'	real part of E^* (storage modulus)
E''	imaginary part of E^* (the loss modulus)
F	force
F_b	buoyancy force
F_s	force associated with surface tension
F_c	capillary attachment force during bubble nucleation
F_p	foam production under sparging
F_{p^*}	foam production under agitation
G_{ad}	adsorption energy
G	Gibbs coefficient of elasticity
H_i	initial foam height
H_r	residual foam height
H_f	foam height
H_{equ}	equilibrium foam height (Bikerman test)
H_{of}	immersion depth of orifice tube
H_{og}	Oswald coefficient of gas solubility
h	thickness of liquid foam film
h_i	initial thickness of foam film
h_t	final thickness of foam
h_{tr}	transitional thickness of foam film
h_F	height of foam as defined in test method
h_s	height of solution as defined in test method
h_{st}	thickness change due to loss of stability
h_m	minimum film thickness for bubble coalescence
h_w	thickness of aqueous thin film core
h_{ml}	thickness of adsorbed monolayer adsorbed on thin film
h_w	equivalent thickness of a liquid film
h_{cr}	critical thickness of film rupture
$h_{cr,bl}$	critical thickness of film rupture via black spots formation
J	diffusion and transfer of soluble surfactant to bubble interface
J_s	flow of surfactant along surface of bubble
K_n	equilibrium constant for dissociation of mono-species into aggregates
K	gas permeability
K_m	diffusion coefficient
K_f	electro-conductivity of foam
K_s	specific conductivity of foam
K_{dc}	ratio of foam drainage time to coarsening time (t_{dr}/t_c)
k_f	gas permeability of monoatomic and diatomic atoms
$k_n{}^o$	dimensionless permeability
k_o	coefficient of background permeability
k_{ml}	diffusion coefficient of single surfactant monolayer
k_s	specific electrical conductivity of bulk solution
k_f	electroconductivity of foam

K_c	dimensionless number (PB permeability)
k_{eff}	effective coefficient of gas transfer
L_{pb}	Poisson border length (foam structure)
L	length of foam train (permeability model)
l_t	length of foam film
l_c	length of surfactant hydrocarbon chain
N_f	number of flips in Hele-Shaw cell
n	number of bubbles
n_f	intervening films in foam train model (standing diffusion model)
P	pressure
P_l	liquid pressure
P_g	gas pressure
P_B	Laplace pressure in Plateau borders
P_c	capillary pressure
$P_c{}^{max}$	maximum value of the capillary pressure
P_f	packing parameter for solid particles at bubble surface
Q_l	liquid flow rate
Q_g	gas flow rate (cm^3/s)
R_b	radius of bubble
R_{pb}	Poisson Boltzman curvature (foam structure)
R_t	radius of shrinking bubble
R_f	radius of film curvature
r_b	radius of bubble or a microscopic film
r_{equiv}	equivalent sphere radius
r_o	radius of orifice
r_f	film radius
R_g	radius of gyration
S_o	solubility of gas in liquid
S_c	spreading coefficient
T	absolute temperature
T_c	cycle of period $1/f$
T_d	drainage time of thin liquid film between two discs
T_{TR}	Threshold of entry barrier
t	time
t_d	coalescence time (MTR theory)
t_s	thin film stability time
t_b	thin film breakage time
t_{in}	thin film inertia time
t_{att}	attachment time (particle and bubble interaction)
t_i	induction time (particle and bubble interaction)
t_r	thin film rupture time (particle and bubble interaction)
t_{tpc}	three-phase contact time (particle and bubble interaction)
t_p	bubble transition or persistence time (coalescence)
t_{dev}	time of deviation (foam test methods)

t_{tr}	time of transition (foam test methods)
$t_{1/2}$	half-life of foam (foam test methods)
t_{dr}	drainage time
t_c	foam coarsening time
V	volume of gas
V_b	volume of bubble
V_o	initial foam volume
V_i	initial volume of foam
ΔV^F	change if foam volume (foam test methods)
ΔV^S	change in volume of drained liquid (foam test methods)
V_h	volume of hydrocarbon chain
V_{end}	final volume of foam produced (surfactant depletion experiments)
V_d	foam decay rate
V_{sgf}	superficial gas flow rate
V_L	liquid drainage velocity
V_{ab}	bubble approach velocity
V_{Re}	Stefan–Reynolds drainage rate between two discs
V_{FD}	forced drainage velocity
K_p	bubble persistence constant
j_g	superficial gas flow (humidity and evaporation)
K_H	Hilgenfeldt ratio of drainage time to coarsening
v	liquid flow velocity
V_{av}	average approach velocity between two bubbles
V_{brs}	bubble rise velocity
V_{ch}	bubble approach velocity (Chester Hofman)
V_k	bubble approach velocity (Klaseboer)
V_{y1}, V_{y1}	bubble approach velocity (Yaminsky)
V_{cav}	critical bubble approach velocity
U	average rate of foam decay
U_g	superficial gas flow rate (m/s)
U_{term}	terminal velocity of bubble
U_{max}	maximum velocity of bubble
U_d	foam decay rate
W	work
W_e	Weber number
W_{cr}	critical value of Weber number
W	volume % liquid content of foam (foam test methods)
W_l	volume % liquid content of foam (conductivity test methods)
W_l	width of liquid inlet channel in microfluidic cell
W_g	width of gas inlet channel in microfluidic cell
x, y	coordinates in direction to the interface
z	coordinate normal to the interface
β	dynamic contact angle
Γ	adsorption, surface concentration

Γ_∞	maximum adsorption, surface concentration
Γ	surface excess (adsorbed)
Γ_R	relative adsorption
Γ_{max}	maximum amount of coverage of surfactant
γ	surface or interfacial tension
γ_o	surface or interfacial tension of a pure solvent system
γ_{dyn}	dynamic surface tension
γ_{equ}	equilibrium surface tension
η	dynamic viscosity
η_d	surface dilational viscosity
η_{sh}	surface shear viscosity
η_d	viscosity of dispersion
η_o	viscosity of liquid matrix
$1/\kappa$	Debye screening length
λ	characteristic tube width to bubble radius
Π	disjoining pressure
Π_{el}	electrostatic component of the disjoining pressure
Π_{vw}	van der Waals component of the disjoining pressure
Π_{st}	steric component of the disjoining pressure
Π_{osc}	oscillatory component of the disjoining pressure
ρ_l	density of liquid
ρ_g	density of gas
ρ_R	ratio density (wet and dry foam)
$\sum$	Bikermann unit of foaminess
τ	micellar break-up time
$\tau_{1/2}$	lifetime of a foam film or foam
θ	equilibrium contact angle
Φ_l	volume fraction of liquid or wetness of foam
Φ_g	volume fraction of gas fraction
$\Phi_{g,critical}$	critical gas fraction
φ_s	volume fraction of dispersed solid
χ	bubble shape deformation factor
ω	angular frequency
Ψ_o	surface potential

Constants

A_H	Hamaker constant
A_R	retarded Hamaker constant
F	Faraday constant
g	gravitational constant
k_B	Boltzmann constant
K_n	dissociation constant

N_A	Avogadro number
R_g	ideal gas constant
R_e	Reynolds number
T	absolute temperature

Abbreviations

BCP	block copolymer
CBF	common black film
CMC	critical micelle concentration
CPP	critical packing parameter
DLVO	Derjaguin, Landau, Verwey, Overbeek theory
FTT	film trapping technique
HLB	hydrophilic/lyphophile balance
MTR	Manev–Tsekov–Radoev theory
NBF	Newton black film
POE	polyethylene oxide
RH	relative humidity
WP	Weaire-Phelan (foam cell structure)