

## 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 different 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.

# Bubble and Foam Chemistry

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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, *Foamsplex*, 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.

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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R. J. Pugh

## 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)
$k_{\text{eff}}$	effective coefficient of gas transfer
$L_{\text{pb}}$	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
$P_c^{\text{max}}$	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 ( $\text{cm}^3/\text{s}$ )
$R_b$	radius of bubble
$R_{\text{pb}}$	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
$r_{\text{equiv}}$	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
$T_{\text{TR}}$	Threshold of entry barrier
$t$	time
$t_d$	coalescence time (MTR theory)
$t_s$	thin film stability time
$t_b$	thin film breakage time
$t_{\text{in}}$	thin film inertia time
$t_{\text{att}}$	attachment time (particle and bubble interaction)
$t_i$	induction time (particle and bubble interaction)
$t_r$	thin film rupture time (particle and bubble interaction)
$t_{\text{tpc}}$	three-phase contact time (particle and bubble interaction)
$t_p$	bubble transition or persistence time (coalescence)
$t_{\text{dev}}$	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
$\Delta V^F$	change in foam volume (foam test methods)
$\Delta V^S$	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)
$W_1$	volume % liquid content of foam (conductivity test methods)
$W_1$	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
$\beta$	dynamic contact angle
$\Gamma$	adsorption, surface concentration

$\Gamma_{\infty}$	maximum adsorption, surface concentration
$\Gamma$	surface excess (adsorbed)
$\Gamma_{\text{R}}$	relative adsorption
$\Gamma_{\text{max}}$	maximum amount of coverage of surfactant
$\gamma$	surface or interfacial tension
$\gamma_{\text{o}}$	surface or interfacial tension of a pure solvent system
$\gamma_{\text{dyn}}$	dynamic surface tension
$\gamma_{\text{equ}}$	equilibrium surface tension
$\eta$	dynamic viscosity
$\eta_{\text{d}}$	surface dilational viscosity
$\eta_{\text{sh}}$	surface shear viscosity
$\eta_{\text{d}}$	viscosity of dispersion
$\eta_{\text{o}}$	viscosity of liquid matrix
$1/\kappa$	Debye screening length
$\lambda$	characteristic tube width to bubble radius
$\Pi$	disjoining pressure
$\Pi_{\text{el}}$	electrostatic component of the disjoining pressure
$\Pi_{\text{vw}}$	van der Waals component of the disjoining pressure
$\Pi_{\text{st}}$	steric component of the disjoining pressure
$\Pi_{\text{osc}}$	oscillatory component of the disjoining pressure
$\rho_{\text{l}}$	density of liquid
$\rho_{\text{g}}$	density of gas
$\rho_{\text{R}}$	ratio density (wet and dry foam)
$\Sigma$	Bikermann unit of foaminess
$\tau$	micellar break-up time
$\tau_{1/2}$	lifetime of a foam film or foam
$\theta$	equilibrium contact angle
$\Phi_{\text{l}}$	volume fraction of liquid or wetness of foam
$\Phi_{\text{g}}$	volume fraction of gas fraction
$\Phi_{\text{g,critical}}$	critical gas fraction
$\varphi_{\text{s}}$	volume fraction of dispersed solid
$\chi$	bubble shape deformation factor
$\omega$	angular frequency
$\Psi_{\text{o}}$	surface potential

### Constants

$A_{\text{H}}$	Hamaker constant
$A_{\text{R}}$	retarded Hamaker constant
$F$	Faraday constant
$g$	gravitational constant
$k_{\text{B}}$	Boltzmann constant
$K_{\text{n}}$	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/liphophile balance
MTR	Manev–Tsekov–Radoev theory
NBF	Newton black film
POE	polyethylene oxide
RH	relative humidity
WP	Weaire-Phelan (foam cell structure)