

Surfactants

In Solution, at Interfaces and in Colloidal Dispersions

Bob Aveyard

OXFORD GRADUATE TEXTS

SURFACTANTS

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OXFORD

UNIVERSITY PRESS

Great Clarendon Street, Oxford, OX2 6DP, United Kingdom

Oxford University Press is a department of the University of Oxford. It furthers the University's objective of excellence in research, scholarship, and education by publishing worldwide. Oxford is a registered trade mark of Oxford University Press in the UK and in certain other countries

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First Edition published in 2019

Impression: 1

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Published in the United States of America by Oxford University Press 198 Madison Avenue, New York, NY 10016, United States of America

> British Library Cataloguing in Publication Data Data available

Library of Congress Control Number: 2019937511

ISBN 978-0-19-882860-0

DOI: 10.1093/oso/9780198828600.001.0001

Printed and bound by CPI Group (UK) Ltd, Croydon, CR0 4YY

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Preface

Surfactants are ubiquitous in nature and have been known, made and used by man for millennia. They adsorb from aqueous solution to various kinds of interfaces, and if sufficiently concentrated in solution, they simultaneously aggregate into sub-microscopic units (*micelles*). This ability to adsorb and to aggregate makes surfactants enormously useful in many industrial processes and in a wide range of everyday products.

The behaviour of surfactants in solution and at interfaces (i.e. *surfactant science*) comes under the broad umbrella of colloid science which, as whole, underwent a renaissance in the second half of last century. It is now very much an accepted academic subject, although not as widely taught as it might be given its importance to the understanding and control of many technological and biological processes. It underpins and is part of the relatively new nanoscience and nanotechnology. Insights into basic surfactant science have been exploited extensively in industry, and what was once empirical 'know how' (of say formulators) has become increasingly informed by the underlying science.

In the main, colloid science has been served well by academic texts, although the basic aspects of surfactant science have been less extensively covered. As mentioned, surfactant behaviour has direct relevance to a range of chemical technologies, for example, those involved in the production of foodstuffs, personal care and household products, pharmaceuticals, agrochemicals, and so on, and much of what has been written is directed primarily to the practical and industrial application of surfactants. Consequently there is room for a pedagogical text covering some of the more fundamental aspects of the physical science of surfactant behaviour, at a level suitable for senior undergraduates and postgraduates in chemistry and the allied disciplines of physics, chemical engineering, food science, pharmacy and biological and medical sciences. It is hoped that this book will help towards meeting such a need, and at the same time be of use to researchers in industry faced with the need to familiarize themselves with some background aspects of surfactant behaviour.

In writing the book, it has been assumed that the reader has a knowledge of basic physical chemistry, particularly chemical thermodynamics, and of simple physics (e.g. electrostatics). Mathematics (elementary algebra and calculus) is kept at a simple level, consistent with the straightforward derivation of many of the equations presented. Where an equation is simply presented, a reference to an original research paper is usually given. There are some well-established textbooks which are referred to throughout the book, but the majority of the references made are to original research papers in the scientific literature. These relate to the examples discussed in the text, and in this way the reader will be able to gain a wider appreciation of the subject matter.

A novel feature of the book is a section entitled 'Themes and Connections'. The way in which the material has been assembled and broken into chapters is to some extent

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arbitrary since topics can often be grouped in a variety of useful ways, depending on the interests of the reader. In part this is catered for in the text by providing cross references, and of course connections can be made by referring to the book index. However, in order to help the reader a little more explicitly, a series of major topics has been selected and relevant material to be found throughout the book is referred to under the topic headings. A student of surface chemistry or a research worker embarking on an industrial project involving the use of surfactants, or indeed someone assigned to produce a university or industrial course in surface chemistry or surfactant science, may wish to understand in a general way something about, for example, interfacial tension, capillarity, the curvature properties of surfactant monolayers or wetting, spreading and thin liquid films. The material referred to under a given topic (which is illustrative rather than exhaustive) is what might have been included in a chapter devoted to that topic alone. It is hoped that the presentation of some of the material in this way will help to give the reader a broader and more coherent understanding of the subject matter.

Increasingly, small and colloidal particles are being used as (in place of) surfactants, for example in the stabilization of emulsions. As background to the use of particles as quasi surfactants, chapters are included covering the adsorption of single particles and the formation of particle monolayers at fluid interfaces (Chapter 17) and aspects of the use of particles in the stabilization of (Pickering) emulsions (Chapter 18).

Although colloid and surfactant science gained 'respectability' rather late in the day, their scientific foundations have had contributions from a number of great scientists over the centuries. To reflect this, short biographical notes are given throughout the text in recognition of the contributions of such scientists as Newton (intermolecular forces), Franklin (early experiments on insoluble monolayers), Faraday (early preparation and recognition of colloidal dispersions), Plateau (behaviour of collections of soap films in foams), and Gibbs (thermodynamics of surfaces).

I am most grateful to John Clint, Paul Fletcher, and Brian Vincent for reading the manuscript of the book and making valuable and constructive suggestions. Of course the responsibility for errors, misconceptions and omissions lies entirely with me. I have learned much of the surfactant science I know alongside, and often from my friends and co-research workers at Hull University over the years, particularly Bernie Binks, John Clint, Paul Fletcher, Tommy Horozov, and Vesko Paunov. Thanks to them, as well as to all the Ph.D. students and postdoctoral research workers I have had the pleasure of working with. Last and by no means least, my thanks go to my wife for her great forbearance during the preparation of the book.

Bob Aveyard Beverley, December 2018

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Principal symbols

The equation or section numbers refer to the place where the symbol first appears or is defined.

я	surface area §3.2
A	Helmholtz free energy §4.2.2; area per mol or per molecule §5.3
A_o	molecular co-area §5.3.2
A_{σ}	Helmholtz free energy per unit area of surface (4.2.16)
A	Debye–Hückel constant §4.3.3
A_H	Hamaker constant (11.2.3) (subscript H is omitted if phase subscripts used)
а	activity (4.3.6); (subscript) denotes air §3.2; area available to head group at micelle surface §9.4
aw	(subscript) denotes air/water interface
ao	optimal head group area §9.5.1
a_{\pm}	mean ionic activity §4.3.3
ads	(subscript) denoting adsorption
b	neutron scattering length density of adsorbed molecule §5.5.2
С	molar concentration; curvature §10.2.2
с _К	critical coagulation concentration §13.2
C ₀	spontaneous curvature §10.2.2
D	diffusion coefficient §6.2.2
d	(superscript) denoting from dispersion forces §3.3
d	(subscript) denoting liquid drop §3.4.2
d	distance of closest approach of centres of molecules §5.3.2; surfactant layer thickness §5.5.2; crystal spacing (9.11.3)
d_o	equilibrium separation of centres of molecules §5.3.2
Ε	electric field §A10.1; entry coefficient (12.3.1)
Ec	curvature energy of surface, area \mathcal{A} (10.2.9)

E^{g}	generalized entry coefficient (12.3.3)
e	mathematical constant
e ⁻	electronic charge
F	force
F_u	free energy of forming unit area plane surface from droplets §10.2.2
f	activity coefficient
f(x)	normal Gaussian) distribution §9.10
finter	force of interaction between 2 spherical particles (17.4.2)
f^{s}	activity coefficient in surface (5.5.10)
f_{\pm}	mean ionic activity coefficient §4.3.3
G	a Gibbs free energy (4.2.9)
G	Gibbs free energy §2.1; shear modulus §6.2.1
G^*	complex modulus (15.1.5)
G'	storage (elastic) modulus (15.1.6)
G''	loss (viscous) modulus (15.1.6)
g	acceleration due to gravity
g _c	curvature energy per unit area (10.2.1)
$g(\tau)$	correlation function in dynamic light scattering (A10.8)
Η	enthalpy §2.1; mean curvature (10.2.11)
h	Planck constant; separation between surfaces (11.2.3)
Ι	intensity (light, scattered neutrons) §A10.1
Ι	ionic strength §4.3.3
I(Q)	intensity of scattered neutrons (A10.11)
i	(subscript) generic component label
$\mathcal{J}(t)$	shear creep compliance (15.1.4); Janus balance §17.3.2
j	flux §6.3.1
Κ	equilibrium constant §9.2.1
k	Boltzmann constant
k^{-}	rate constant for monomer dissociation from micelle (9.10.1)
k_H	Huggins coefficient (15.3.5)

l	(subscript) denoting liquid
т	molality
mic	(subscript) denoting micelle formation §9.2.1
Ν	number of molecules/ions
$N(\infty)$	number density in bulk solution (5.3.28)
n	number of moles §2.1; neutron refractive index (8.1.2); refractive index §8.3; aggregation number §9.2.1; diffraction order (9.11.3); number molecules per unit volume (11.2.4)
n ^o	ion number concentration in bulk solution (11.2.15)
n^+	number concentration of cations (11.2.15)
n¯	number concentration of anions (11.2.15)
ñ	complex refractive index (8.3.6)
n _{agg}	aggregation number defined in (9.5.2)
N_A	Avogadro number
0	(superscript) denotes standard quantity §2.1
oa	(subscript) denotes oil/air interface
ow	(subscript) denotes oil/water interface
Р	wetting perimeter §A3.1; packing factor (9.5.4)
P(Q)	form factor (A10.2)
p	(superscript) denoting from polar forces §3.3
Þ	pressure; vapour pressure §3.4.2; polydispersity index (10.2.8)
рс	capillary pressure §12.2.2
p^{o}	saturated vapour pressure §3.4.2
p(n)	micellar size distribution (9.4.10)
Q	momentum transfer (modulus of the wave vector) (8.1.1) and (A10.4)
q	heat absorbed by system (4.2.1); charge
q_{im}	image charge (17.4.1)
R	gas constant
$R_{ heta}$	Rayleigh ratio §A10.1
R_G	radius of gyration of a particle (A10.3)
R(Q)	reflectivity §5.2.2

R_H	hydrodynamic radius (A10.7)
R	molar ratio water: aggregated surfactant in droplet §10.1.2
r_g	radius of gyration of polymer molecule §11.3.3
<i>r</i> *	radius of critical nucleus §3.4.2
S	classical spreading coefficient §(16.2.1); entropy (4.2.2)
S^{g}	generalized spreading coefficient (16.2.8)
\$	(superscript) denoting use of surface phase model §4.1.1
sa	(subscript) denotes solid/air interface
so	(subscript) denotes solid/oil interface
STU	(subscript) denotes solid/water interface
Т	temperature
T_m	average micellar lifetime (9.10.7)
t	time
t_r	relaxation time in Maxwell model (15.2.6)
trans	(subscript) denoting transfer between phases §5.3.1
U	internal energy (4.2.1)
V	volume; interaction energy between 2 molecules (A5.3)
V(h)	interaction energy per unit area between surfaces, separation h (11.2.3)
V_A	attractive interaction energy per unit area between surfaces §11.2.1
V_R	repulsive interaction energy per unit area between surfaces §11.2.3
V_T	$V_A + V_R $ §11.2.4
V_S	steric interaction energy per unit area §11.3.1
V_{Sm}	osmotic contribution to steric interaction energy §11.3.1
V_{dep}	attraction energy from depletion forces §11.3.3
v_p	volume of particle (A10.11)
v_m	molar volume of liquid §3.4.2
υ	subscript denoting vapour §3.4.2; molecular volume §9.4; neutron velocity (A10.10); drop velocity (14.6.3)
vol	(subscript) referring to Volmer model (5.3.23)
W_A ; W^A	work of adhesion $3.3 - W^A$ is used when phase subscripts are present
WC	work of cohesion §16.2.1

W	hydration interaction energy (11.3.8)
τυ	work done on system (4.2.1); interaction energy between molecules Box 11.7
x	mol fraction; fraction of bulk phase concentrations $5.5.1$; number of nearest neighbour sites per site (A5.3)
z	valence of an ion
	Greek symbols
α	a phase label §2.1; van der Waals interaction parameter (5.3.25); ratio of concentrations §5.5.3 and §9.7; compound excluded area §5.5.4; micellar degree of dissociation (9.6.2); polarizability of molecule (11.2.2); angle indicating extent of apolar cap on spherical Janus particle §17.3.1
α_c	micellar degree of dissociation (9.6.4)
α_p	degree of surfactant dissociation at plane surface (9.6.5)
β	a phase label $\S2.1$; interaction parameter in regular solution theory (5.5.17); interaction parameter (5.5.18)
Г	surface concentration
Γ^{s}	surface concentration §4.1.1.
Γ^{σ}	surface excess concentration §4.1.2
$\Gamma_2^{(1)}$	relative adsorption of component 2 (4.3.5)
γ	surface or interfacial tension (3.2.1)
γc	interfacial tension at the cmc §10.2.4; critical surface tension (16.3.9)
γ^d	part of interfacial tension arising from dispersion forces §3.3
γ_{f}	film tension (12.1.1)
γ^p	part of interfacial tension arising from polar forces §3.3
Ϋ́	shear or strain rate §6.2.1
γ	shear strain §6.2.1
$\dot{\gamma}^*$	complex shear strain rate (15.2.1)
Δ	change in thermodynamic quantity §2.1; ellipsometric parameter (8.3.5)
$\Delta \chi$	surface potential Box 5.5
δ	amount of nonionic surfactant §10.4.2; adsorbed polymer layer thickness §11.3.1; phase angle §15.1; lens angle §16.2.3
δ_{rs}, δ_{rp}	phase shift on reflection of s and p -polarized components (8.3.2)

ε	permittivity; Gibbs elasticity Box 12.2
ε _o	permittivity of free space
ε_r	relative permittivity
ε^*	dilational modulus (6.2.4); complex dilational viscoelastic modulus (6.2.8)
ε'	storage (elastic) modulus (6.2.8)
ε''	loss modulus (6.2.8)
η	viscosity
η^*	complex viscosity (15.1.9)
η_d	surface dilational viscosity (6.2.5)
η_s	surface shear viscosity (6.2.2)
η_r	relative viscosity (15.3.1)
η_P	plastic viscosity §15.4.3
η_{sp}	specific viscosity (15.3.3)
$[\eta]$	intrinsic viscosity (15.3.4)
θ	angle; contact angle §3.3; fractional surface coverage §7.4
θ_A	advancing contact angle §16.3.2
θ_{CB}	Cassie–Baxter contact angle (16.3.22)
θ_R	receding contact angle §16.3.2
θ_W	Wenzel contact angle (16.3.21)
θ_a	contact angle of apolar part of Janus particle with oil/water interface §17.3.1
θ_c	contact angle at $\tau = \tau_c $ §17.2.2
θ_m	contact angle at $\tau = \tau_m $ §17.2.2
θ_p	contact angle of polar part of Janus particle with oil/water interface $\$17.3.1$
$(\theta_p)_t$	value of θ_p at which particle transfers from water to oil (17.3.3)
κ	bending elastic modulus §10.2.2; reciprocal of double layer thickness (11.2.20)
$\overline{\kappa}$	Gaussian elastic modulus §10.2.2
λ	wavelength §5.5.2
λ_c	critical wavelength (12.4.1)
μ	chemical potential §2.1; apparent viscosity §15.1
ν	frequency of oscillation §6.2.2
ve	absorption frequency in UV (11.2.10)

- ξ persistence length (10.2.12); ratio of adsorptions §16.3.4
- π spreading or surface pressure §4.4
- Π osmotic pressure (11.2.26)
- Π_D disjoining pressure (11.3.7)
- Π_{el} electrical contribution to disjoining pressure (11.6.8)
- ρ density of a bulk phase §3.4.1; neutron scattering length density §5.5.2; complex amplitude reflection ratio (8.3.1); volume charge density (11.2.16); number density of particles §11.3.4
- Σ specific surface area (of a solid) §7.1
- σ surface charge density §5.3.2;(superscript) denoting use of Gibbs model for surface §4.1.2; (subscript) denoting per unit area of surface §4.2.2; standard deviation of micelle size §9.10.1
- τ surface thickness §4.1.1; shear stress §15.1; line tension §16.2.3
- τ_c relaxation time §6.2.2
- τ_1 fast micelle relaxation time (9.10.1)
- τ_2 slow micelle relaxation time §9.10.2
- τ_{12} slow micelle relaxation time (9.10.5)
- τ_B Bingham yield stress (15.4.3)
- τ_c critical line tension §17.2.2
- τ_m maximum line tensions §17.2.2
- $\overline{\tau}$ reduced line tension (17.2.2)
- ϕ correction factor in drop volume method §A3.3; phase §10.4.1
- φ correction factor in du Noüy ring method §A3.1; phase shift (6.2.7); volume fraction
- χ Flory-Huggins parameter §11.3.1
- ψ electrical potential; ellipsometric parameter (8.3.4); meniscus slope angle §12.4.3
- ω angular velocity §A3.5; angular frequency §6.2.2; partial molar surface area (4.2.18)
- ω_c characteristic frequency §6.2.2

Section I Background

Section I comprises the first three chapters of the book. The chemical nature of surfactants, what they can do, and why they are important are described in the first chapter. A characteristic of surfactant molecules is that, as a result of their amphipathic nature, they adsorb from water to a variety of interfaces and aggregate in aqueous solution. These key processes are often energetically driven by the removal of the hydrophobic groups in the molecule from water. In Chapter 2 the antipathy between nonpolar molecules and groups and water is explored. Capillarity, wetting, and interfacial tension are the subjects covered in Chapter 3. These are relevant to many aspects of behaviour in systems containing surfactants as well as to the varied applications of surfactants.

What are surfactants?

1.1 The nature of surfactants

Surfactants...today you have probably eaten some or rubbed others on your bodies in one form or another. Plants, animals (including you), and microorganisms make them. Many everyday products contain surfactants or surfactants have been involved during their manufacture. So what are they, how do they behave in solution, at interfaces, and in colloidal dispersions, and why are they useful? This is the subject of the book.

The term surfactant is a contraction of *surf* ace *active agent*, and surfactants are so called because they adsorb at surfaces (interfaces). The tendency to adsorb arises from the dual (amphiphilic) nature of surfactant molecules, which contain a hydrophobic moiety (the 'tail' group, which is often an alkyl chain) attached to a hydrophilic ('head') group. A surfactant molecule can be represented for present purposes, as shown in Fig. 1.1a. In Fig. 1.1c a single layer (*monolayer*) of surfactant molecules is shown adsorbed at an air/water or oil/water interface. The driving force for the adsorption arises either from the removal of the surfactant tails from water (for surfactant originally in water) or the removal of the heads from (nonpolar) oil if the molecules were originally in the oil. In either case, in the monolayer the heads are in aqueous surroundings and the tails are out of contact with bulk water. Since, for example, long chain alkanes are virtually insoluble in water, the water-solubility of surfactant molecules arises from the very favourable interaction of the head groups with water (through dipole–dipole and/or ion–dipole interactions). The chemical nature of some typical head groups is covered in §1.3.

Adsorption of molecules at a surface or interface (Box 1.1) always lowers the surface or interfacial tension (Chapter 4). If the concentration of surfactant in an aqueous phase is sufficiently high, and when the adsorbed monolayer is effectively full (i.e. *close-packed*), some of the molecules in solution aggregate into *micelles* (or other aggregates), which remain in equilibrium with adsorbed molecules and un-aggregated molecules (in the context usually termed 'monomers') in the aqueous phase, as discussed in Chapter 9. The concentration at which micelles just begin to form is termed the *critical micelle concentration* (*cmc*) (§9.1). A cross-section of, for example, a simple spherical micelle is represented in Fig. 1.1b; the hydrophobic tails form the core of the micelle, which is liquid-like, while the heads are at the surface of the micelle in contact with water. The

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Figure 1.1 (a) Representation of a surfactant molecule; (b) cross-section of a spherical micelle in water; (c) an adsorbed monolayer at an air/water or oil/water interface.

diameter of such a micelle is approximately (but less than) twice the extended surfactant molecular length (say 3 or 4 nm), and very approximately a spherical micelle might contain of the order of a hundred molecules. Micelles are able to take up ('*solubilize*') water-insoluble materials. At the *cmc*, the adsorbed monolayer is close-packed (Box 1.2) and the lowering of surface tension by the surfactant adsorption is maximum and roughly constant. Because surfactants lower surface and interfacial tension, adsorb at interfaces, and solubilize materials in micelles they are extremely useful in a very wide variety of products, systems, and processes.

Box 1.1 Interface and interfacial tension

Interfacial tension is defined as the work required to form unit area of an equilibrium interface at constant temperature, pressure, and volume, as explained in §4.1. It quantifies the tendency of an interface to contract; small free drops of liquid for example are spherical in shape, the sphere having the minimum area (hence minimum surface free energy) for a given volume of liquid. Adsorption at an interface always lowers interfacial tension. The term *surface tension* is often used for an interface between a condensed and a vapour phase, whereas *interfacial tension* is frequently taken to refer to the region between two condensed phases. In general however, an interface is an area over which two phases (in any physical state, solid, liquid, or gas) are in contact. Physically it has a finite thickness and contains material from each of the contacting phases (Chapter 4).

Box 1.2 What does 'close-packed' mean?

The term *close-packed* simply implies that no further adsorption occurs into the monolayer with increasing bulk concentration of surfactant. The area available per adsorbed molecule in the close-packed state is not however simply related to a molecular dimension as represented

Box 1.2 Continued

by say a molecular model (see 5.3.2 and 9.5.1). In the present context close-packing corresponds to the condition where the chemical potential of surfactant is the same for surfactant in the monolayer and in micelles, which are in equilibrium with single surfactant molecules in solution.

1.2 Where are surfactants encountered?

Over the centuries, and probably back to ca. 3000 bc, the most commonly encountered surfactant was undoubtedly soap, which is an alkali metal (usually sodium) salt of a carboxylic acid. Soap can be prepared from animal fats or vegetable oils, which contain mixtures of triglycerides, together with lye (containing sodium hydroxide) obtained by extraction from plant ashes. The process of the alkaline hydrolysis of fats and oils is called saponification; the term possibly arises from the name of the Italian town Savona where soap was manufactured as early as the ninth century ad. The French for soap is savon.

Various plants known to our ancestors produce natural surfactants; for example, saponins (natural glycosides) can be extracted from the foliage of soapwort. Our bodies produce natural surfactants or surfactant-like molecules, perhaps the most obvious being lung surfactants (Box 1.3). Our livers produce bile acids, the salts of which are biological surfactants. Phospholipids (e.g. lecithin) are produced by the liver and are founds in cell membranes. Lecithin is also used in the production of food emulsions (e.g. ice cream), since it is a very effective emulsifying agent. Bacteria produce biosurfactants (§1.3.5).

Box 1.3 Lung surfactants

Lung, or pulmonary, surfactants are present in alveolar surfaces within the lung and consist of a mixture of phospholipids and proteins. The mixture is very surface active (i.e. adsorbs very strongly) at the surfaces of the alveoli and reduces their interfacial tension. Thus the production of lung surfactant makes it possible to expand alveolar surfaces easily on inhalation. In a condition termed respiratory distress syndrome (RDS), which affects 10% of premature infants and which is life-threatening, the lungs do not produce sufficient lung surfactant without which the lungs are unable to inflate.

Soap is a good cleaning agent, but it produces a precipitate or scum when used in hard water because the calcium and magnesium carboxylates are water-insoluble. New synthetic surfactants were introduced in the 1920s which do not suffer in this way and now there are many types of surfactants available for a whole range of applications and formulations. As will be seen they can, for example, act as emulsion stabilizers (Chapter 14), promote wetting of surfaces (Chapter 16), produce foaming (Chapter 14), effect the dissolution and dispersion of 'water-insoluble' material in water

6 What are surfactants?



Figure 1.2 Some of the things surfactants can do and examples of their applications.

(Chapter 9), and stabilize dispersions of solid particles against flocculation (Chapter13). As a result of this remarkable versatility, surfactants are used in industries ranging from agrochemical through pharmaceutical to crude oil production and processing. The worldwide surfactant industry is a multi-billion pound business. In 2014, for example, the global consumption was 17,500 kilotons, over half of which was used in household detergent formulations. Other significant amounts were used in industrial and institutional cleaning, production of personal care products, oil production, in the textile industry, food manufacture, mineral production, and pulp and paper manufacture (see Fig. 1.2).

1.3 Types of surfactant and their classification

Although soaps (originating from renewable vegetable and animal fats) are still significantly used, the present market is dominated by products derived from petrochemicals, notable amongst these being alkylbenzene sulfonates and alkylphenol ethoxylates. Modern detergent powders typically contain linear alkylbenzene sulfonates. Nonetheless, there is now pressure to use renewable plant feedstocks more and reduce the use of nonrenewable petrochemicals. In this connection, the use of 'sugar surfactants' is becoming important; these are made from carbohydrates and plant oils and find use as emulsifiers in foodstuffs and cosmetics. Alkyl polyglucosides are used in detergent products.

Surfactants are usefully classified in terms of the nature of their hydrophilic head group, which can be nonionic, ionic, or zwitterionic (amphoteric) (Tadros, 2005). Ionic surfactants can of course be anionic or cationic. Polymeric surfactants form another class. In addition fluorocarbon surfactants constitute an important group of speciality surfactants which are particularly effective in lowering the surface tension of water. Perfluoroalkyl chains form the tail of fluorocarbon surfactants, which can have ionic, nonionic or amphoteric head groups.

In what follows just a few examples of the various types of surfactants are given. Authoritative and fuller accounts can be found, for example, in books by Porter (1994), Holmberg et al. (2003), Holmberg (2003), Rosen and Kunjappu (2012), and Tadros (2005).

1.3.1 Nonionic surfactants

The hydrophilic moieties in nonionic surfactants are commonly polyoxyethylene groups, which if attached to a straight alkyl chain hydrophobe gives rise to so-called alcohol ethoxylates: $C_nH_{2n+1}(CH_2CH_2O)_mOH$. The formula is often contracted to C_nE_m , where *n* and *m* represent the tail and head group lengths, respectively. If *n* is relatively small and *m* is relatively large, it is clear for these surfactants that the head group can be considerably larger that the tail group. Alcohol ethoxylates have often been used in academic investigations of the behaviour of nonionic surfactant solutions since pure monodisperse samples can be prepared with a range of both *n* and *m* values. Alkylphenol ethoxylates, in which the hydrophobic groups are alkylphenol residues rather than straight alkyl chains, are widely used as heavy duty degreasing detergents.

Mono-, di-, and triesters of sorbitan with carboxylic acids (e.g. octadecanoic acid, oleic acid) form an important group of nonionic surfactants, often referred to as Spans (an Atlas trade name). These materials can be ethoxylated giving so-called Tweens; Spans are insoluble in water whereas Tweens are usually water-soluble. The surfactants (see Fig. 1.3) are used as cosmetics emulsifiers and in pharmaceutical preparations.



Figure 1.3 (a) A sorbitan ester, where R is H or an alkyl chain. If, for example all $R = C_{18}H_{37}$, the structure is that of Span 65. (b) An example of an ethoxylated sorbitan ester, termed a Tween.



Figure 1.4 A dodecyl polyglycoside.

As mentioned, surfactants with head groups based on carbohydrates are becoming of more importance. In addition to sorbitan, glucose and sucrose for example can be esterified giving respectively alkyl polyglycosides (APGs, used in detergents) (Fig. 1.4) and sucrose esters (used in food manufacture). Surfactants of this type are often referred to generically as 'sugar surfactants'.

1.3.2 Ionic surfactants

Anionic surfactants

The alkali metal carboxylates (soaps) have already been referred to and have long been produced. Soaps are cheap, easily made and biodegradable, but their alkaline earth metal salts are insoluble in water and produce a scum. Animal fats and plant oils are used in their production, giving alkyl chain lengths above 10 and below 20. Shorter chains render the soaps too soluble in water and longer chains result in insolubility in water, although the long chain homologues become oil-soluble. The alkali metal soaps are used (particularly in developing countries), for example, in toilet soap and other personal care products, in cutting oils, ore flotation, and emulsion polymerization.

Sulfonates and sulfates are the most commonly encountered anionic surfactants (Fig. 1.5). The sodium salts of linear alkylbenzene sulfonates are very widely employed in industrial and household detergent formulations. Other cations can be used and surfactants based on amine salts (e.g. of triethanolamine, isopropylamine) have found uses in dry-cleaning and production of agricultural emulsions. A very widely encountered alkyl sulfate is sodium dodecylsulfate (SDS), which is both industrially important and widely used in academic studies. SDS is used, for example, in low temperature detergents, in toothpaste, and in food and cosmetic emulsions.

To make the sulfates and sulfonates more water-soluble and increase their resistance to precipitation in electrolyte solutions, ethyleneoxy (EO) groups can be incorporated giving, for example, an alcohol ether sulfate $R(CH_2CH_2O)_xSO_4^-M^+$ (*x* is say 2 or 3). Addition of EO groups to carboxylates (producing $RO(CH_2CH_2O)_xCH_2COO^-$) can also render the Ca²⁺ and Mg²⁺ salts more water-soluble.

An anionic surfactant worth mentioning here, which has been used widely in academic studies (see Chapter 10), is Aerosol OT (sodium di(2-ethylhexyl)sulfosuccinate) (Fig. 1.6).

Cationic surfactants

Cationic surfactants are widely encountered in everyday life. Since the head group carries a positive charge, cationics tend to adsorb at solid/water interfaces which usually



Figure 1.5 Top: Sodium dodecylsulfate. Bottom: An isomer of sodium p-dodecylbenzene sulfonate.



Figure 1.6 Structure of Aerosol OT; R represents the 2-ethylhexyl group.



Figure 1.7 Hexadecyltrimethylammonium bromide (CTAB).

carry a negative charge (but see Chapter 7). The most common examples of cationic surfactants are the quaternary ammonium salts mono-, di-, and trimethylammonium halides. Cetyltrimethylammoniun bromide (usually abbreviated to CTAB) has been widely used in fundamental studies of surfactant behaviour (Fig. 1.7). Cetyl is the common name for the hexadecyl group; the single-chain surfactants usually have chain lengths between 8 and 18. The dialkyl chain surfactants are of course less water-soluble than the single chain surfactants for a given chain length. Other cationic head groups are possible, as for example in dialkylbenzylammonium chlorides, used in disinfectants. Cationics are also employed *inter alia* in hair conditioners and as antistatic agents.

1.3.3 Amphoteric surfactants

Amphoteric surfactants carry a pH-dependent charge; the charge is positive at low pH and negative at high pH. At some intermediate pH, the so-called *isoelectric point* (*i.e.p.*), the head group is net neutral. At high pH amphoteric surfactants behave as anionic surfactants, at low pH like cationics and at the *i.e.p.* like nonionics. The aqueous-phase solubility is minimum at the *i.e.p.* Amphoteric surfactants are widely used in non-irritant



Figure 1.8 Top: β -N-decylaminopropionic acid (isoelectric point pH = 4). Bottom: N-alkylbetaines are zwitterionic above the i.e.p. and cationic below, but are never anionic.

mild detergent products such as shampoos and bath products. Some examples of amphoteric surfactant types are shown in Fig. 1.8. Some zwitterionic surfactants, for example, sulfobetaines, $RN^+(CH_3)_2(CH_2)_xSO_3^-$ (where *x* is the number of methylene groups in the molecule), are not sensitive to pH.

1.3.4 Polymeric surfactants

So-called polymeric surfactants do not always have very high molecular weights, and some might be better termed oligomeric surfactants. Block copolymers of ethylene oxide (EO) and propylene oxide (PO) are important examples of polymeric surfactants, for example, the simple ABA type $(EO)_x(PO)_y(EO)_x$. The EO and PO moieties are, respectively, hydrophilic and hydrophobic in nature. Relative molar masses range from about 1000 to 30,000, and these materials can be tailor made with different amounts of EO and PO for different applications. Uses include pigment dispersants in latex paints (high molar mass members with high EO content), and petroleum demulsifiers and foam control agents (low molar mass and low EO content) (see Chapter 14).

Graft copolymers, in which side chains are grafted onto a polymeric backbone, form an important group of both natural and synthetic surfactants. The backbone can be hydrophobic with hydrophilic side chains or vice versa. The backbone can also contain both hydrophilic and hydrophobic groups (so the backbone might be considered a block copolymer) and both hydrophilic and hydrophobic side chains can be attached simultaneously to the backbone. As can be appreciated many variations are possible (Holmberg et al., 2003), but a common feature in polymeric surfactants is that the molecules can be so oriented as to present hydrophilic groups to aqueous surroundings and hydrophobic groups to a nonpolar region (e.g. the oil at an oil/water interface). An example of a polymeric surfactant with a hydrophilic backbone and hydrophobic side chains is hydrophobized starch (an emulsion stabilizer and 'associative thickener'); there are many surfactants with a hydrophobic backbone and hydrophilic side chains, including ethoxylated alkyd resins and the important class of silicone surfactants. The siloxane backbone in silicone surfactants is the hydrophobe; silicone polyethers (Fig. 1.9.) are commonly used surfactants which can contain one or more polyoxyalkylene chains (e.g. polyoxyethylene or polyoxypropylene) attached to the backbone.



Figure 1.9 A silicone polyether surfactant.

From what has been said so far it is clear that the use and importance of surfactants is very wide indeed. Improvements in performance are always being sought, as are novel structures for traditional as well as for emerging commercial and research uses. Given this, it is a little difficult to fit, in an explicitly useful way at least, all surfactant types of interest into the above simple classification. For this reason some surfactant types which have been of more recent interest, namely biosurfactants and *gemini* and *bolaform* surfactants, are mentioned below. In addition, small solid particles are known to adsorb, often very strongly, at fluid/fluid interfaces (Chapter 17). It has long been known that particles can stabilize emulsions in the absence of surfactants (Chapter 18), and there is now a growing interest in using particles in place of surfactants for some uses.

1.3.5 Biosurfactants

Many microorganisms produce amphiphilic materials termed biosurfactants. The surfactants are formed on cell surfaces or excreted into the surroundings. There is a wide variety of structures of biosurfactants, often complex, with either high or low molar mass. Many have been purified and identified, whilst others have been detected by the effect they have on the surface tension of water. High molar mass biosurfactants are usually polymeric hetero-saccharides containing proteins whilst those with low molar masses are commonly glycol-lipids, the hydrophilic groups being based on trehalose, sophorose, or rhamnose. Examples, together with space filling models, are given in Fig. 1.10.

A widely studied example of a lipopeptide biosurfactant is surfactin (from *Bacillus subtilis*). It has the structure shown in Fig. 1.11, the hydrophilic group being made up of seven amino acids. The versatile behaviour illustrates the considerable potential of biosurfactants in a number of areas. Surfactin is an antibiotic and has antifungal and antiviral properties; it also has potential in crude oil recovery (enhanced oil recovery, EOR) and environmental applications. Biosurfactants are probably best known for their potential in bioremediation of polluted soil. The surfactants, which can be added to soil or created *in situ*, increase the dispersion (and/or solubility) of hydrocarbon based contaminants and hence their bioavailability to bacteria which break down the pollutants to less harmful products. Biosurfactants are less toxic and more readily biodegradable than conventional synthetic surfactants and are likely to find many uses (Banat et al., 2000), for example in the production of pharmaceuticals, toiletries, and paints.



Figure 1.10 Examples of glycolipid biosurfactants based on (left) sophorose and (right) rhamnose. In space-filling models the red spheres represent the O atoms. In the model of the rhamnolipid surfactant (bottom right) the two heptyl chains are at the top/back of the molecule.



Figure 1.11 The lipopeptide biosurfactant, surfactin. In the molecular model the alkyl chain is on the middle right. Red atoms are oxygen and blue are nitrogen atoms.

1.3.6 Gemini and bolaform surfactants

Gemini¹ surfactants form a relatively new class of surfactants (Zana, 2002) and are essentially surfactant dimers in which two monomers are joined by a spacer group at or close to the head groups. The most commonly studied Gemini surfactants have been the di-cationic quaternary ammonium materials of the kind shown in Fig. 1.12. The example is a dimer of decyltrimethylammonium bromide ($C_{10}TAB$) joined by a

¹ Gemini is the constellation containing the stars Castor and Pollux, the so-called 'heavenly twins'. A bola is a missile used in South America consisting of two heavy balls one at each end of a rope.



Figure 1.12 An example of a di-cationic Gemini surfactant, designated 10-3-10 (see text).

trimethylene spacer. The general designation of this kind of Gemini surfactant is n-s-n, where n represents the hydrophobic chain length and s the spacer group chain length. The hydrophilic moiety in Gemini surfactants can be anionic or nonionic as well as cationic and it is possible also to have asymmetric surfactants where the two hydrophobic chains are of different lengths.

Gemini surfactants are of particular interest for several reasons. The cmc (§1.1) of a simple Gemini surfactant can be 1–2 orders of magnitude less than that of the constituent monomer. For example, for the 12-3-12 surfactant of the type shown in Fig. 1.12 the cmc is 0.055 wt per cent whereas that for the monomer dodecyltrimethylammonium bromide is 0.5 wt per cent. Since the surface tension of an aqueous solution at the cmc is at its lowest, for a given concentration of a Gemini surfactant is very much greater than that for the constituent monomer. In addition, aqueous solutions of Gemini surfactants with short spacer groups at concentrations above the cmc can give solutions with high viscosity and viscoelasticity (Chapter 15). This arises from the shape of the micelles which can be worm-like and become mutually entangled in solution. Gemini surfactants are produced commercially.

Bolaform surfactants are related structurally to Gemini surfactants in that they have two hydrophilic head groups, one at each end of a spacer, but the spacer is much longer than in Gemini surfactants. Thus Gemini surfactants are monomers joined at (or close to) the head groups, whereas bolaform surfactants can be considered to be monomers covalently joined through their chains. The head groups can also have hydrophobic tails attached but the spacer group is significantly longer than the tail length. The head groups can be the same or different. Whereas Gemini surfactants are synthetic, bolaform surfactants can be produced biologically in the membranes of bacteria. The surfactants are able to span and confer stability on the membranes. Examples of bolaform surfactants are given in Fig. 1.13.

1.3.7 Small solid particles as surfactants

Dispersions of very small particles in water do not exhibit all the types of behaviour associated with surfactants; for example, they do not aggregate in solution in the same way that surfactant molecules do, although they may flocculate. What they usually do very well however is adsorb at the surface of water or at oil/water interfaces (Chapter 17). A given particle may, for example, be more wetted by water than by oil. It is observed



Figure 1.13 Bolaform surfactants. Both examples are of unsymmetrical surfactants and both contain a cationic head group. The example below has one head group based on a sugar moiety.



Figure 1.14 A spherical particle resting at an oil/water interface. The particle is more wetted by water than by oil so that the angle θ (the contact angle) is less than 90°.

nevertheless that it can be strongly adsorbed from water to the oil/water interface, where part of the particle obviously resides in oil rather than water. It turns out that the driving force for adsorption is the removal of liquid interface (circular area \mathcal{A} in Fig. 1.14). The interfacial tension of a surface is the work required to *form* unit area of that interface; this work is regained if the interface is *removed*.

It has long been known that solid particles can stabilize emulsions (Chapter 18), but it is only relatively recently that particle adsorption and monolayer properties have been sufficiently well-understood to tailor make particles with the required properties (e.g. surface wettability) for the production of emulsions. It is likely that particles will be increasingly used rather than surfactants for the stabilization of certain kinds of emulsions in the future. Silica particles (with diameters of only a few nm) can be prepared with the required wettability for various uses, and of course silica is chemically inert and hence environmentally friendly.

GENERAL BIBLIOGRAPHY

A selection of supplementary resources, that cover some of the same subject matter as the present book, is given below. There are a number of texts that, unlike the present book, are directed primarily to more applied aspects of surfactant behaviour.

- S. Abbott, *Surfactant Science Principles & Practice*. DEStech Publications, Inc., 2018. This is a stimulating presentation and technical resource aimed in the main at industrial formulators; it is available free online. A nice interactive feature is that formulae have links to apps so you can see how graphs change with input values.
- T. Cosgrove (ed.), Colloid Science: Principles, Methods and Applications. Blackwell Publishing, Oxford, 2005.

A useful book (288 pages) of contributed chapters based on a spring school on colloid science given by the Bristol Colloid Centre in the UK. It covers colloids, surfactants, and polymers.

- E. Dickinson, An Introduction to Food Colloids. Oxford University Press, Oxford, 1992. A short (207 pages) introductory text. The book covers some areas in common with the present book, at a little lower level but with great insight. There is of course a focus on areas appropriate for food scientists.
- D. F. Evans and H. Wennerström, *The Colloidal Domain Where Physics, Chemistry and Biology Meet.* 2nd edition. Wiley-VCH, Weinheim, 1999.

This book of 630 pages is a classic treatment of colloid science theory, methods, and applications for advanced students and researchers in industry. The level is higher and more detailed, and the approach more mathematical than that in the present book.

J. Goodwin, *Colloids and Interfaces with Surfactants and Polymers*, 2nd edition. Wiley, Chichester, 2009.

An introduction (280 pages) to fundamental colloid science with less emphasis on surfactant systems than in the present text.

- K. Holmberg, B. Jőnsson, B. Kronberg, and B. Lindman, *Surfactant and Polymers in Aqueous Solution*, 2nd edition. John Wiley and Sons Ltd, Chichester, 2003. Surfactants are often used together with polymers to impart required properties to a formulation, and this valuable book considers polymer+surfactant systems from a practical rather than theoretical standpoint.
- J. N. Israelachvili, *Intermolecular and Surface Forces*, 3rd edition. Academic Press, 2011. The behaviour of colloidal systems is intimately associated with the operation of surface forces, and this monograph covers the theories and concepts of such forces. It is the standard work on the subject and is presented at a level suitable for students and research workers. Jacob Israelachvili, who died in September 2018, contributed immeasurably to our understanding of surface forces and the ways in which they operate.
- D. Myers, *Surfactant Science and Technology*, 3rd edition. Wiley-Interscience, New York, 2006. A well-regarded introduction (400 pages) to surfactants, surface activity, and surfactant applications. It is aimed primarily at beginners and non-specialists who seek a practical knowledge of surfactant systems.

16 What are surfactants?

M.J. Rosen and J.T. Kunjappu, *Surfactants and Interfacial Phenomena*, 4th edition. Wiley, 2012. A standard text (616 pages), now in its 4th edition, on the properties and applications of surfactants. Intended for industrial chemists as well as for teaching purposes, it has a minimum of mathematical treatment and contains very useful tables of collected data on surfactants.

A number of books by T.F. Tadros cover various aspects of surfactant and colloid behaviour in a range of systems:

- (a) Books published by Walter de Gruyter GmbH & Co KG:
- Basic Theory of Interfacial Phenomena and Colloid Stability, 2018; Basic Principles of Interface Science and Colloid Stability, 2017; Basic Principles of Formulation Types, 2018; Industrial Applications I: Pharmaceuticals, Cosmetics and Personal Care, 2017; Pharmaceutical, Cosmetic and Personal Care Formulations, 2018; Polymeric Surfactants: Dispersion Stability and Industrial Applications, 2017; Emulsions: Formation, Stability, Industrial Applications, 2016; An Introduction to Surfactants, 2014.
- (b) Books published by John Wiley and Sons:
- Colloids in Agrochemicals, 2009; Formulation of Disperse Systems, 2014; Emulsion Formation and Stability, 2013; Dispersion of Powders in Liquids and Stabilization of Suspensions, 2012; Colloids in Paints, 2011; Self-Organized Surfactant Structures, 2011.
- (c) Published by Wiley-VCH Verlag:

Colloid Stability and Application in Pharmacy, 2007.

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Oil and water do not mix—hydrophobic hydration

2.1 The thermodynamic parameters of dissolution of a solute in water

The poor solubility of nonpolar groups in water provides the driving force for, amongst other processes, adsorption of surfactants from aqueous solution to air/water and oil/water interfaces (Chapter 5), and for micelle formation (Chapter 9). It is useful therefore to have some insight into the way in which hydrocarbon molecules and moieties interact with water.

Imagine the dissolution, at constant temperature T and pressure p, of one mole of a solute X, originally in the form of an ideal gas (phase α , containing only X) to give an ideal dilute solution in water (phase β). Since both phases are ideal dilute systems, there are no X-X interactions in either phase, and in the aqueous phase the only interactions are those between water and molecules of X. The chemical potentials of X in phases α and β , μ_X^{α} and μ_X^{β} respectively, are defined as

$$\mu_X^{\alpha} = \left(\partial G^{\alpha} / \partial n_X^{\alpha}\right)_{T,p}; \quad \mu_X^{\beta} = \left(\partial G^{\beta} / \partial n_X^{\beta}\right)_{T,p,n_B}$$

where G are the Gibbs free energies of the superscripted phases. The n_X are numbers of moles of X in the phases denoted by the superscripts. The solvent (water) is denoted B. Differences in the chemical potentials are responsible for the spontaneous flow of the solute between the two phases until equilibrium is attained. The molar free energy of transfer of X from α to β , $\Delta_{max}^{\alpha \to \beta} \mu$, is

$$\Delta_{trans}^{\alpha \to \beta} \mu = \mu_X^{\beta} - \mu_X^{\alpha} \tag{2.1.1}$$

At distribution equilibrium (i.e. when the aqueous phase is saturated with X under the prevailing conditions) the two chemical potentials are equal and $\Delta_{trans}^{\alpha \to \beta} \mu$ is zero.

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There are two contributions to chemical potential μ , one arising from the concentration (number density), *c*, of the solute and the other, μ^{o} , which is associated with the interactions of a solute molecule with its local surroundings:

$$\mu_X^{\alpha} = \mu_X^{o,\alpha} + RT \ln(c_X^{\alpha}/c_X^{s,\alpha}); \ \mu_X^{\beta} = \mu_X^{o,\beta} + RT \ln(c_X^{\beta}/c_X^{s,\beta})$$
(2.1.2)

Here, μ^{o} are *standard* chemical potentials and $c_X^{s,\alpha}$ and $c_X^{s,\beta}$ are the concentrations of X in the α and β phases in their respective *standard states*. Usually the c_X^s are chosen as unity (in the same units used for c_X) and in which case they are omitted from the expressions for μ in (2.1.2). Then, the standard chemical potential of the solute is equal to its chemical potential when its concentration is unity, that is, when it is in its standard state.

From (2.1.1) and (2.1.2), taking standard concentrations of X of unity in both α and β

$$\Delta_{trans}^{\alpha \to \beta} \mu = \Delta_{trans}^{\alpha \to \beta} \mu^{o} + RT \ln \left(c_X^{\beta} / c_X^{\alpha} \right)$$
(2.1.3)

where $\Delta_{trans}^{\alpha \to \beta} \mu^o = \mu_X^{o,\beta} - \mu_X^{o,\alpha}$. From what has been said, $\Delta_{trans}^{\alpha \to \beta} \mu^o$ contains that part of $\Delta_{trans}^{\alpha \to \beta} \mu$ that arises from the interactions of the solute with water accompanying dissolution.¹ At equilibrium $\Delta_{trans}^{\alpha \to \beta} \mu = 0$ and so, from (2.1.3)

$$\Delta_{trans}^{\alpha \to \beta} \mu^o = -RT \ln \left(c_X^\beta / c_X^\alpha \right)_{equ}$$
(2.1.4)

The ratio $\left(c_X^{\beta}/c_X^{\alpha}\right)_{equ}$ is called the Ostwald absorption coefficient. Corresponding changes in standard entropy, enthalpy and heat capacity that accompany dissolution can be obtained from the temperature dependence of $\Delta_{trans}^{\alpha \to \beta} \mu^o$ using the usual thermodynamic relationships.

2.2 Hydrocarbons are only sparingly soluble in water—hydration of CH₂ groups

Many surfactants contain hydrocarbon moieties as the hydrophobic groups, and the driving force for the transfer of these groups from water to a nonpolar or vapour environment arises in some way from the antipathy between the hydrocarbon groups and water. A water molecule and a methylene group (the constituent unit of say an alkyl chain) are of similar size and the dispersion forces (see §11.2.1) operating between the pairs H_2O and H_2O , CH_2 and CH_2 , and H_2O and CH_2 are expected to be similar,

¹ In addition, $\Delta_{trans}^{\alpha \to \beta} \mu^{o}$ also depends on the choice of standard states in phases α and β , as can be appreciated from the text.

and are attractive in nature. The antipathy arises therefore from effects other than the straightforward operation of intermolecular dispersion forces. Since water has a degree of tetrahedral structure at room temperature, imposed by hydrogen bonding, introduction of a nonpolar solute might be expected to cause a disruption of the local water structure in some way. The transfer of an alkane molecule from the vapour phase to water would therefore be expected to be accompanied by a more positive entropy change than for transfer to a non-structured nonpolar liquid. In fact, the entropy change is found to be large and *negative*, and in addition, the (positive) changes in heat capacity are anomalously high.

The beginnings of a modern understanding of the origins of the hydrophobicity (hence low solubility in water) of hydrocarbons were given in a landmark paper by Frank and Evans in 1945. They wrote: 'When a rare gas atom or nonpolar molecule dissolves in water at room temperature, it modifies the water structure in the direction of greater "crystallinity"; the water, so to speak, builds a microscopic iceberg around it... As the temperature is raised these icebergs melt giving rise to the enormous partial molar heat capacity of these gases in water.'

Standard free energies of solution in water, $\Delta_{trans}\mu^o$, of some normal alkane vapours at room temperature (relative to that for ethane) are plotted against the alkane chain length in Fig. 2.1. It is noted that the methylene group increment denoted $\Delta_{hyd}\mu^o$, which is positive, is independent of the choice of standard states (assuming the *same* standard states are chosen for all systems) and represents the hydration free energy of a methylene group. This increment and those in the corresponding enthalpy and entropy, $\Delta_{hyd}H^o$ and $\Delta_{hvd}S^o$, at room temperature, are given in Table 2.1.



Figure 2.1 Standard free energies of solution (relative to that for ethane) of linear alkane vapours in water at room temperature. The free energies increase linearly with increasing alkane chain length.

Table 2.1 Thermodynamic parameters for the hydration (at 293 K) and adsorption (from vapour to the air/water surface at 285.6 K) of the methylene group. Free energies and enthalpies are given in kf mol⁻¹ and entropies in f mol⁻¹ K⁻¹

$\Delta_{hyd}\mu^{o}$	$\Delta_{hyd}H^{o}$	$\Delta_{hyd}S^{o}$	$\Delta_{ads}\mu^{o}$	$\Delta_{ads}H^{o}$	$\Delta_{ads}S^{o}$	
+0.7	-2.8	-11.7	-2.0	-4.4	-8.4	

Both the enthalpy and entropy of hydration are temperature dependent, and at room temperature the *positive* increment per CH₂ in $\Delta_{hyd}\mu^{o}$ ($\approx +0.7$ kJ mol⁻¹) arises from the effect of the entropy of hydration ($-T\Delta_{hyd}S^{o} \approx +3.5$ kJ mol⁻¹ CH₂ whereas the corresponding $\Delta_{hyd}H^{o}$ is ≈ -2.8 kJ mol⁻¹). At elevated temperatures the contributions of enthalpy and entropy to the free energy of hydration are reversed, with favourable contributions coming now from the entropy of hydration and unfavourable changes being contributed by the enthalpy change. This temperature dependence is reflected in the changes in hydrocarbon solubility with temperature; solubilities pass through a minimum in the region of 310–350 K.

The original picture of microscopic 'icebergs' surrounding nonpolar moieties in water has often been considered to be an over-simplification. Certainly there have been difficulties with the use of direct physical techniques (e.g. neutron scattering and EXAFS) to probe the water structure around dissolved nonpolar molecules because the concentration is, due to the low solubility in water, necessarily low. Nonetheless, nonpolar moieties in molecules containing polar groups (e.g. alkanols) can be probed, although of course the vicinity of a polar group to the nonpolar moieties within the molecule can complicate matters. Some experimental studies have led to the suggestion that the 'structure' induced by nonpolar groups is less ordered than ice and not dissimilar to that in liquid water remote from a dissolved molecule, and that the 'order' may be associated with the orientation (rather than disposition) of water molecules close to nonpolar solute molecules. Recently, however, Grdadolnik et al. (2017), based on IR studies of nonpolar molecules (including methane and ethane) in HDO water, claim that water hydrogen bonding close to the nonpolar solutes is strengthened and that the water displays extensive structural ordering similar to that in clathrates, supporting the original ideas of Frank and Evans (1945). Interested readers should also consult the extensive work of Soper on water structure in water and aqueous solutions (e.g. Soper, 2014).

Whatever the details of the origins of hydrophobic hydration (and the story is probably not yet finished), it is clear that around room temperature hydrophobic moieties perturb water in such a way as to lead to a large negative change in entropy (giving a positive contribution to the free energy) when the groups are introduced into water. Conversely, when hydrophobic groups are removed from aqueous surroundings, in such processes as adsorption of surfactants from aqueous solution and micelle formation in water, there is a negative free energy contribution arising from the dehydration of the nonpolar moiety.

When hydrocarbon groups are in close proximity in aqueous solution, they can become loosely associated by so-called *hydrophobic bonding*, a term introduced by Kauzmann (1959). The total amount of unfavourably perturbed water around two dissolved nonpolar groups is reduced as the two groups mutually approach. This gives rise to a solvent mediated attraction, although 'bonding' might not be a very good term for this. Much of the interest in hydrophobic bonding has arisen out of work on protein folding (Kauzmann, 1959; Tanford, 1997). The hydrophobic side chains of proteins in water undergo mutual hydrophobic bonding which is one of the factors influencing the shape of the protein molecules in aqueous solution.

What has been discussed above applies at molecular length scales to nonpolar groups and molecules in water. It is well known however that there are also strong attractive interactions between *macroscopic* hydrophobic surfaces in water, which can extend over large separations between surfaces. Various possible origins of such forces have been considered and in Chapter 11 these and a variety of other so-called *surface forces* are described.

2.3 How do nonpolar groups interact with water at a water surface?

In a close-packed monolayer of surfactant at the air/water interface it may reasonably be assumed that the surfactant tails are disposed roughly normal to the interface, as illustrated in Fig. 1.1. When surfactant adsorbs to form a very dilute monolayer at the air/water surface however, it is not immediately obvious what the disposition of the alkyl chains might be. Are the chains repelled or attracted by the water *at the surface*? If the surfactant tails can lie along the surface without unfavourably perturbing the local water structure, then it might be expected that the chains would orient in some way parallel to the surface, thereby interacting with the water through van der Waals forces. On the other hand, if the water is unfavourably disrupted by the presence of the nonpolar groups (as it is in *bulk* water) it may be that they coil as much as possible so avoiding contact with the interfacial water. These two extreme possibilities are illustrated schematically in Fig. 2.2.

An idea of the orientation of adsorbed surfactant chains can be obtained by considering the standard thermodynamic parameters of adsorption of a series of normal alkanes from dilute vapour to the air/water interface. The way in which the standard free energy of adsorption, $\Delta_{ads}\mu^o$, is calculated from the lowering of the surface tension with increasing gas pressure (concentration) is discussed in §4.3. The quantity $\Delta_{ads}\mu^o$ per methylene group is analogous to the hydration free energy, $\Delta_{hyd}\mu^o$, discussed in §2.2 and given in Table 2.1, but now the hydrocarbon is present in an infinitely dilute monolayer rather than in an infinitely dilute bulk aqueous solution.

Standard free energies and enthalpies of adsorption, together with $T\Delta_{ads}S^o$ for a series of normal alkanes at 285.6 K are shown in Fig. 2.3.² For clarity, values are given relative



Figure 2.2 Schematic representation of a surfactant molecule at the air/water surface. (left) Molecule disposed with chain parallel to the interface and (right) coiled and roughly normal to the interface.

 2 The chosen standard state for the alkanes in the surface is a little complicated, but is the same for all the alkanes. The increment per methylene group under these circumstances is independent of the standard state. The standard state for the vapour phase is one atmosphere.



Figure 2.3 Standard thermodynamic parameters for the adsorption of normal alkanes at 285.6 K from dilute vapour to the air/water surface. Values are given relative to those for pentane.

to those for pentane. It is evident that the free energies, enthalpies and entropies of adsorption all become more negative with increasing alkane chain length. Incremental values per methylene group are given in Table 2.1, and compared with corresponding values for hydration of the methylene group. It is seen that, although the hydrocarbon moieties interact unfavourably with bulk water, they are attracted by water at an air/water interface, and so it is likely that adsorbed alkane molecules assume orientations that are essentially parallel to the interface.

The (negative) entropy of adsorption per CH_2 group could possibly be accounted for by changes in conformation of the alkanes accompanying adsorption, together with vibrations normal to the surface. The enthalpy change probably arises in the main from the operation of dispersion forces between alkane and water molecules at the interface. This can be appreciated by considering the enthalpy of *cohesion*, $\Delta_{cohesion}H$, of liquid alkanes. As will be discussed in §3.1, the free energy (work) of cohesion is defined as the isothermal work of creating two units of area of liquid surface, that is, $\Delta_{cohesion}G =$ 2γ where γ is the surface tension. Enthalpies of cohesion can then be obtained from the temperature variation of the free energies in the usual way. The cohesion parameters relate to unit area; to convert them to molar quantities per CH_2 it is only necessary to obtain a surface area, σ_{CH_2} , occupied by a methylene group at the alkane surface. This can be approximated by the area occupied in the plane of aligned alkane molecules in bulk liquid alkane. The distance between the long axes of the chains is about 0.47 nm and the C–C distance resolved along the chain is 0.126 nm, giving σ_{CH_2} of about 0.06 nm². From surface tensions of alkanes as a function of temperature, and σ_{CH_2} , an enthalpy of cohesion for the methylene group of about 3.8 kJ mol⁻¹ is obtained. This relates to *separating* alkane from alkane; bringing two surfaces together (i.e. destroying the surfaces) is associated with an enthalpy change of -3.8 kJ mol⁻¹. This figure is reasonably close to the molar enthalpy of adsorption of the methylene group, -4.4 kJ mol⁻¹. Since only dispersion forces are operative in alkanes, this implies that the enthalpy of adsorption of alkanes could arise largely from dispersion forces between water molecules and alkanes; it is recalled that the dispersion forces acting between H_2O and CH₂ groups are expected to be similar to those between two CH₂ groups.

In conclusion, it is not necessary to invoke the notion of water 'structure' being perturbed by hydrocarbon groups at the surface of water. This is in contrast to the situation in bulk water, where such a perturbation is implicated in the very low solubility of hydrocarbons in water.

2.4 Concluding remarks

Many surfactants contain alkyl chains as the hydrophobic moiety, and adsorption from aqueous solution to air/water and oil/water interfaces (Chapters 4 and 5), as well as micelle formation (Chapter 9) are driven at least in part by changes in the local environment of the hydrophobic group. The methylene group is a basic unit of an alkyl chain and consideration has therefore been given above to the changes in free energy that result from changes in environment of the CH_2 group. Discussion was centred on the ways in which the methylene group interacts with water, both in bulk aqueous solution and at the air/water surface. The relative free energies of the methylene group in various environments that relate to adsorption and micelle formation are shown schematically in Fig. 2.4.

For the systems represented in Fig. 2.4, the most positive free energy is that for the CH₂ group in ideal dilute aqueous solution. This leads to the low solubility of alkanes in water. The difference in free energy for the group in water and in ideal dilute vapour is the hydration free energy, which as discussed is positive $(0.7 \text{ kJ mol}^{-1})$. The difference in free energy of the methylene group in aqueous solution and at the air/water interface, that is, the adsorption free energy, is about -2.7 kJ mol^{-1} , which is less than that when the group is adsorbed to the oil/water interface (ca. -3.2 kJ mol^{-1}) (see §5.3.1). The methylene group free energy is similar for a group at the oil/water interface (where it



Figure 2.4 Schematic representation of the free energy of a methylene group in various environments. The micelle interior, bulk liquid alkane, and oil at the oil/water interface are similar, but not equivalent, and the energy in these environments is indicated by a band.

dips into the oil phase), in a micelle interior (which is liquid-like, §9.3) and in bulk liquid alkane. With reference to the figure, the free energy of micellization is ca. $-3.1 \text{ kJ mol}^{-1} \text{ CH}_2$, and that of condensation into bulk liquid alkane is $-3.0 \text{ kJ mol}^{-1} \text{ CH}_2$.

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3

Capillarity, wetting, and surface (interfacial) tension

3.1 Capillarity

From everyday experience it is known that, for example, a porous cloth will absorb water and that a watercolour brush will retain paint, in both cases against the action of gravity. It is also observed that a plane surface of a liquid becomes distorted when it comes into contact with, say, a vertical solid surface. Tea in a teacup forms a meniscus where it meets the surface of the cup, and in this case the (wetting) liquid in the concave meniscus¹ is lifted above the level of the plane liquid surface distant from the side of the cup (Fig. 3.1a). In the case of mercury in a glass bottle or capillary tube (e.g. in a thermometer), the meniscus is convex and the (non-wetting) liquid is depressed rather than elevated (Fig. 3.1b).

If a cylindrical capillary tube (i.e. a tube with a hair-like bore) is placed vertically in a liquid, parts of the meniscus on opposite walls within the tube overlap and the liquid either rises (Fig. 3.2) or is depressed within the tube. The term *capillarity* stems from this



Figure 3.1 (a) A wetting liquid in contact with a vertical solid surface in air; the meniscus is concave and raised above the plane liquid surface. (b) A non-wetting liquid in air in contact with a solid surface. The meniscus is convex and depressed below the plane liquid.

¹ The name *meniscus* derives from the ancient Greek *meniskos* (crescent), a diminutive of *mene*, meaning moon. *Capillus* is the Latin for hair.

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Figure 3.2 *Rise of a wetting liquid, in air, within a capillary tube with internal diameter d and wall thickness D. The angle* θ *which the liquid makes with the tube wall is termed the contact angle. The curved liquid surfaces are termed menisci.*

phenomenon although it also includes other phenomena associated with liquid menisci. For a given liquid, the extent of the rise (*h* in Fig. 3.2) or depression, depends upon the angle at which the meniscus meets the capillary wall, that is, on the *contact angle* θ . The rise also depends on the internal diameter *d* of the tube but not on the wall thickness *D*. The first accurate observations of capillary rise were made by Francis Hawksbee (Box 3.1) in the early part of the eighteenth century.

Box 3.1 Newton, Hawksbee, capillarity, and intermolecular forces

The study of capillarity has been of great importance in the understanding of intermolecular forces. Francis Hawksbee (The Elder) lived from c.1666 to 1713 and was, from 1703 until his death a 'paid performer of experiments' at the Royal Society in London. Supported by Isaac Newton, he was elected Fellow of the Royal Society in 1705. He made accurate observations on capillary rise, and Newton used Hawksbee's findings to gain insights into what at the time were referred to as 'inter-particle' forces. Newton writes about this in his famous work 'Opticks'. The rise of liquids within, for example, capillary tubes was supposed to involve the attraction between particles (i.e. molecules) of the liquid and of the solid. Since, from Hawksbee's experiments it was known that the extent of elevation of the liquid depended only on the internal diameter of the tube and not on the thickness of the walls, it was concluded that the interparticle forces of attraction were short range, involving only those particles close

Box 3.1 Continued

to the solid/liquid interface. At the end of Opticks, Newton wrote a series of Queries. In the last edition of 1730, there are 31 Queries, which are in the form of rhetorical questions, some developing into essays. Query 31 is extensive and begins: 'Have not the small Particles of Bodies certain Powers, Virtues, or Forces, by which they act at a distance...' Later in the Query, having referred to Hawksbee's work on capillary rise, Newton writes concerning forces between particles: 'And therefore where the distance [between particles] is exceeding small, the attraction must be exceeding great... There are therefore Agents in Nature able to make the particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out.' This is a profound observation and the problem is one which continues to exercise physical scientists to the present time.

3.2 Surface and interfacial tension

In order to understand the origins of capillary rise it is convenient to introduce the definition and significance of surface/interfacial tension, γ . As mentioned in Chapter 1 (footnote 1), the term *surface* is often used to refer to the interface between a condensed and a vapour phase, and *interfacial* to the interface between condensed phases; however the term *interface* is general and encompasses the area of mutual contact between phases in any state of matter.

It is a common observation that a small free liquid drop tends to take on an effectively spherical shape. For a given volume, a sphere has the minimum surface area and so it can be inferred that molecules in a surface are in a higher energy state than those in the bulk. Molecules in a condensed phase always possess a net attractive interaction energy due to the balance of attractive and repulsive forces acting in three dimensions. This is why condensation occurs. Molecules at a surface however have negligible energy of interaction with the vapour phase and so work must be done to create a surface, which has an excess free energy compared to (the same amount of) material in bulk. This is why surfaces tend to contract. At the interface between two immiscible or partially miscible condensed phases, α and β , however, the molecules at each of the surfaces of the contacting phases have attractive interaction energies with the surface molecules of the other phase. Surface/interfacial tension is defined as the isothermal reversible work of forming a unit area of interface, and the interfacial tension $\gamma_{\alpha\beta}$ between two condensed phases is less than (or possibly equal to) the sum of the two surface tensions γ_{α} and γ_{β} , as is shown in ((12.3.2)). The excess free energy of molecules at a surface gives rise to a lateral tension within the surface, and Thomas Young (in 1805) noted that, mechanically, an interface behaves as if a (fictitious) uniformly stretched membrane of infinitesimally small thickness existed between contacting phases (Box 3.2). In thermodynamic terms, the surface or interfacial tension, γ , of a material at temperature T and pressure p can be expressed as (see also (4.2.2))

$$\gamma = (\partial G / \partial \mathcal{A})_{T,p,n} \tag{3.2.1}$$

Box 3.2 Thomas Young—a remarkable polymath



Thomas Young, 1773–1829. An English polymath who, amongst other achievements, made important scientific contributions in the fields of light and solid mechanics. World History Archive/Alamy Stock Photo.

Thomas Young (1773–1829) was not only a physicist but also a physician and Egyptologist. He made early discoveries in deciphering Egyptian hieroglyphics such as those on the Rosetta Stone, which was carved in 196 bc (Robinson, 2007). The stone, which is now housed in the British Museum in London, was discovered by French soldiers in Egypt in 1799 in the small town of Rosetta. The French Egyptologist Champollion built upon Young's early work to decipher completely the Rosetta script. As a physicist Young is perhaps most famous for his contributions to the theory of light and of elasticity. In the present context he founded the theory of capillarity in terms of the concept of surface tension (1804). In an article on capillary action appearing in the Encyclopaedia Britannica (1911, volume 5, p. 258), James Clerk Maxwell notes that Young's methods 'though always correct, and often extremely elegant, are sometimes rendered obscure by his scrupulous avoidance of mathematical symbols'. The subject of capillarity was subsequently examined by Pierre Simon Laplace whose results were in many respects identical with those of Young, but were obtained using mathematical methods.

where G is the Gibbs free energy of the system, with surface area \mathcal{A} , containing n mol material. From (3.2.1) the units of γ are seen to be those of energy per unit area, and are frequently quoted in mJ m⁻². Since the excess surface energy results in a tension acting laterally within the surface (hence interfacial *tension*), γ is equivalently defined as the force acting parallel to the surface and at right angles to a line of unit length anywhere within the surface. The dimensions of energy/area are the same as those of force/length, and 1 mJ m⁻² is identical to 1 mN m⁻¹. In some contexts it is convenient to consider interfacial tension as an excess free energy per unit area and in others as a force per unit length. Some values of interfacial tensions for liquid/vapour and water/liquid interfaces,

	liquid/vapour tension	water/liquid tension	−dγ/d <i>T</i> liquid/vapour	−dγ/d <i>T</i> water/liquid
water	72.8		0.16	
decane	23.8	52.3	0.09	0.09
hexadecane	27.4	53.8	0.09	0.09
decanol	28.6	9.0	0.08	0.07
methyl decanoate	28.5	22.5	0.10	0.03

Table 3.1 Some values of surface tension and interfacial tension (against water) of pure liquids that are immiscible or partially miscible with water, at 293.15 K, and their temperature coefficients. Tensions are given in $mN m^{-1}$

Note that the surface tension of water is high relative to that for the other liquids represented. Water has a tetrahedral structure in bulk as a result of hydrogen bonding, and the formation of surface with vapour results in disruption of this structure giving rise to the high surface tension. In contrast, the polar materials decanol and methyl decanoate have surface tensions very similar to that of the alkanes. The polar liquids do not have the extensive bulk structuring that water has and presumably surface molecules can still retain the kind of polar interactions at the surface that are present in bulk. However, as a result of polar interactions with water at liquid/liquid interfaces, the polar materials have lower interfacial tensions with water than do the alkanes.

and their temperature coefficients, are given in Table 3.1. The measurement of interfacial tension for liquid/vapour and liquid/liquid interfaces is described in the Appendix to this chapter.

In the process of capillary rise, an area of solid/air interface is replaced by solid/liquid interface in the capillary tube. Since interfacial tension is the work of forming unit area of interface, it is expected that capillary rise should occur if the interfacial tension between the solid and liquid, γ_{sl} , is less than the tension between solid and air, γ_{sa} . Conversely capillary depression (as with mercury in a glass tube) should occur if $\gamma_{sa} < \gamma_{sl}$. This is considered in a little more detail in the next section, where the topics of wetting and adhesion in relation to the contact angle θ are introduced. For a discussion of the definition of surface/interfacial tension for solid interfaces, see §16.3.3.

3.3 Wetting, adhesion, and the contact angle

Amongst other factors, capillary rise or depression in a capillary, say in air, depends on the contact angle θ that the liquid/air interface makes with the solid/liquid interface. The value of the contact angle is an indication of whether it is energetically favourable for a liquid to contact (wet) the solid (in this case in air) or not. The contact angle shown in Fig. 3.2 for a liquid in a capillary tube is equivalent to the angle that the liquid makes with a smooth flat, horizontal plate of the (same) solid immersed in air, as indicated in Fig. 3.3a. In general it is necessary to stipulate through which phase the angle is measured—the liquid in this case. An (incompletely) wetting liquid has a contact angle less than 90°, whereas a (partially) non-wetting liquid has an angle greater than 90°. Examples of completely wetting liquid-solid pairs ($\theta = 0^{\circ}$) are common whereas completely non-wetting systems ($\theta = 180^{\circ}$) are not (see §16.3.5).

Around a drop with circular cross-section resting on a plane horizontal solid in air, there exists a circular contact line where the three phases, solid, liquid and air meet. With reference to Fig. 3.4, at mechanical equilibrium the forces acting horizontally at a point in the contact line can be resolved to give Young's equation:

$$\gamma_{sa} = \gamma_{sl} + \gamma_{la} \cos \theta \tag{3.3.1}$$

The quantity $\gamma_{sa} - \gamma_{sl} (= \gamma_{la} \cos\theta)$ is referred to as the *wetting tension*.

The *work of adhesion*, W_A , of solid and liquid (in a third medium, say air) is defined as the work associated with parting unit area of solid/liquid interface to give units of area of solid/air and liquid/air interfaces (Fig. 3.5). Thus, noting the definition of interfacial tension, W_A can be expressed in the *Dupré equation*:

$$W_A = \gamma_{sa} + \gamma_{la} - \gamma_{sl} \tag{3.3.2}$$

The interfacial tension of a liquid/fluid interface is readily measurable (see Appendix), but tensions of interfaces involving solids are not, so the expression for W_A in (3.3.2) is not particularly useful. However, combination of (3.3.1) and (3.3.2) gives the more convenient expression for W_A ,



Figure 3.3 Drop of liquid on solid in air with contact angle θ (a) less than 90° and (b) greater than 90°.



Figure 3.4 Forces acting at the contact line of a drop of liquid in air resting on a flat smooth solid surface.



Figure 3.5 Parting a column of solid from a contacting column of liquid with unit interfacial area of tension γ_{sl} to give unit area of solid/air interface, tension γ_{sa} , and unit area of liquid/air interface, tension, γ_{la} .

$$W_A = \gamma_{la} \left(1 + \cos\theta\right) \tag{3.3.3}$$

which is referred to as the Young–Dupré equation. Like γ_{la} , θ is readily accessible experimentally and so W_A can easily be obtained. Values of the work of adhesion of water with some solids in air are given in Table 3.2. As is obvious from (3.3.3) and the table, for a given liquid W_A increases as θ falls, that is, as the liquid increasingly wets the solid.

For capillary rise to occur (Fig. 3.2) the contact angle must be less than 90° ($\cos \theta > 0$), and for capillary depression $\theta > 90^\circ$ ($\cos \theta < 0$). It follows therefore from (3.3.2) and (3.3.3) that in the case of capillary rise $W_A > \gamma_{la}$ and hence $\gamma_{sa} > \gamma_{sl}$. For capillary depression $W_A < \gamma_{la}$ and so $\gamma_{sl} > \gamma_{sa}$, as mentioned at the end of §3.2.

It can be useful to suppose that interfacial tensions are made up of additive components arising from the different kinds of interaction between phases at the interface (Fowkes, 1963). For a polar liquid such as water, the surface tension γ can notionally be split into contributions from dispersion forces, γ^{d} , and 'polar' forces, γ^{p} , arising from dipole interactions and hydrogen bonds, so that

solid	θ through water/°	W_A /mJ m ⁻²		
PTFE	112	45		
hexamethylethane	115	42		
C ₃₆ -paraffin	105	54		
polystyrene	91	72		
cellulose acetate	54	116		

Table 3.2 W_A for water with a range of solids in air at room temperature. The interfacial tension of the air/water interface is taken as 72.8 mN m⁻¹.

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$$\gamma = \gamma^{d} + \gamma^{p} \tag{3.3.4}$$

For say an alkane (1), only dispersion forces are possible so $\gamma_1 = \gamma_1^d$. When an alkane is in contact with water (2) the interfacial tension γ_{12} is the sum of the two surface tensions, γ_1 and γ_2 , *less* a term resulting from the mutual attractive interaction through dispersion forces of the liquids at the interface. Assuming this interaction is the geometric mean, $\sqrt{\gamma_1^d \gamma_2^d}$, the tension in the interfacial region of phase 1 is $\gamma_1 - \sqrt{\gamma_1^d \gamma_2^d}$ and that in 2 $\gamma_2 - \sqrt{\gamma_1^d \gamma_2^d}$ so that γ_{12} is given by

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d}$$
 (3.3.5)

Since the work of adhesion (W_A) between 1 and 2 is $\gamma_1 + \gamma_2 - \gamma_{12}$, it follows that

$$W_A = 2\sqrt{\gamma_1^d \gamma_2^d} \tag{3.3.6}$$

The polar contribution, γ_2^p , to γ_2 can be obtained from measured values of γ_1 , γ_2 and γ_{12} in the following way. Equation (3.3.5) can be recast to give

$$\gamma_2^{\rm d} = (\gamma_1 + \gamma_2 - \gamma_{12})^2 / 4\gamma_1^{\rm d}$$
(3.3.7)

and, noting that $\gamma_1 = \gamma_1^d$, (3.3.6) is used to calculate γ_2^d . The polar contribution γ_2^p is then given as $(\gamma_2 - \gamma_2^d)$. Values of γ^d and γ^p for many liquids are available in the literature. This approach, and elaborations of it, have also been used in the treatment of solid/liquid interfacial tensions, as explained in §16.3.3.

3.4 Curved liquid interfaces: the Young–Laplace and Kelvin equations

3.4.1 The Young–Laplace equation

Many liquid interfaces encountered are curved, as in the case of liquid in menisci of the type already referred to. Examples of particular interest in surfactant science are the surfaces of emulsion and microemulsion droplets. Often, relevant surfaces are spherically curved, as in the case of small emulsion droplets and liquid menisci in sufficiently narrow capillaries. Consider the rise of liquid in air to an equilibrium height h, in a vertical, cylindrical capillary, as depicted in Fig. 3.6. The pressure in the vapour phase is denoted p'' and the very small difference in p'' with height is ignored. The pressure in the liquid within the capillary at the same height as the plane surface of liquid outside the tube, is also p'' at equilibrium. Since the pressure in the liquid column falls with increasing