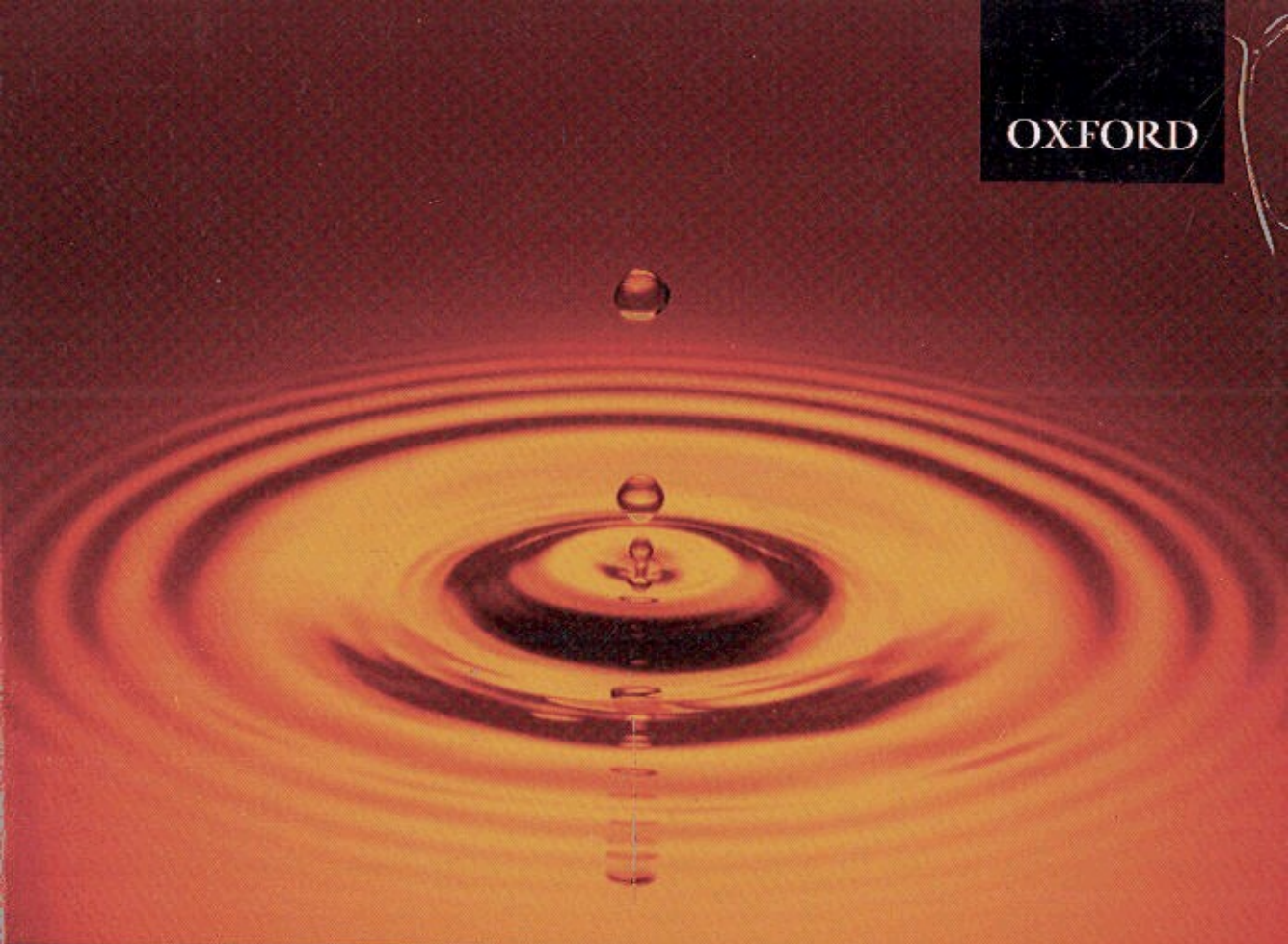


OXFORD



INTERFACIAL SCIENCE

An Introduction

G.T. Barnes
I.R. Gentle

Contents

Preface	v	2.6.2 Capillary rise	17
Acknowledgements	xii	2.6.3 Drop weight or volume	18
Symbols and abbreviations	xv	2.6.4 Maximum bubble pressure	19
		2.6.5 Sessile and pendant drops	20
		2.6.6 Indicator oils	20
Chapter 1			
Introduction	1	2.7 The Laplace equation	21
1.1 The importance of interfaces	1	2.7.1 Applications of the Laplace equation	23
1.2 Surfaces and interfaces	2	2.8 The Kelvin equation	24
1.2.1 Introduction	2	2.8.1 Consequences of the Kelvin equation	25
1.2.2 Types of interface	3	2.8.2 Verification of the Kelvin equation	26
1.2.3 Defining the interfacial region	3	2.9 The surface tension of pure liquids	27
1.3 Stable interfaces	4	2.9.1 Effect of temperature on surface tension	27
1.4 Key concepts	4	2.9.2 The surface tension of liquids	27
1.4.1 Surface tension	5	2.9.3 The hydrophobic–hydrophilic interaction	28
1.4.2 Wetting	5	SUMMARY	30
1.4.3 Adsorption	5	FURTHER READING	30
1.4.4 Emulsions	6	REFERENCES	31
1.4.5 Colloids	6	EXERCISES	31
1.4.6 Membranes	6		
FURTHER READING	6	Chapter 3	
The literature of interfacial science	6	Adsorption and the thermodynamics of surfaces	33
Chapter references	7		
Chapter 2		3.1 Introduction	33
Capillarity and the mechanics of surfaces	8	3.2 Models of the interface	34
2.1 Surface tension	8	3.2.1 The surface phase approach	34
2.2 Work of extension	10	3.2.2 The surface excess properties approach	34
2.3 Contact angle, wetting, and spreading	11	3.3 Adsorption	35
2.4 The surface of tension	14	3.3.1 Adsorption and the dividing surface	35
2.5 Work of adhesion and cohesion	14	3.3.2 Conventions for the dividing surface	36
2.6 Measurement of surface tension	15	3.3.3 Adsorption isotherms	37
2.6.1 Wilhelmy plate	15	3.4 Thermodynamic properties of interfaces	38
		3.4.1 Mechanical work	38
		3.4.2 Internal energy and enthalpy	38
		3.4.3 Gibbs free energy	39

Contents

Preface	v	2.6.2 Capillary rise	17
Acknowledgements	xii	2.6.3 Drop weight or volume	18
Symbols and abbreviations	xv	2.6.4 Maximum bubble pressure	19
		2.6.5 Sessile and pendant drops	20
		2.6.6 Indicator oils	20
Chapter 1		2.7 The Laplace equation	21
Introduction	1	2.7.1 Applications of the Laplace equation	23
1.1 The importance of interfaces	1	2.8 The Kelvin equation	24
1.2 Surfaces and interfaces	2	2.8.1 Consequences of the Kelvin equation	25
1.2.1 Introduction	2	2.8.2 Verification of the Kelvin equation	26
1.2.2 Types of interface	3	2.9 The surface tension of pure liquids	27
1.2.3 Defining the interfacial region	3	2.9.1 Effect of temperature on surface tension	27
1.3 Stable interfaces	4	2.9.2 The surface tension of liquids	27
1.4 Key concepts	4	2.9.3 The hydrophobic–hydrophilic interaction	28
1.4.1 Surface tension	5	SUMMARY	30
1.4.2 Wetting	5	FURTHER READING	30
1.4.3 Adsorption	5	REFERENCES	31
1.4.4 Emulsions	6	EXERCISES	31
1.4.5 Colloids	6		
1.4.6 Membranes	6	Chapter 3	
FURTHER READING	6	Adsorption and the thermodynamics of surfaces	33
The literature of interfacial science	6		
Chapter references	7	3.1 Introduction	33
Chapter 2		3.2 Models of the interface	34
Capillarity and the mechanics of surfaces	8	3.2.1 The surface phase approach	34
2.1 Surface tension	8	3.2.2 The surface excess properties approach	34
2.2 Work of extension	10	3.3 Adsorption	35
2.3 Contact angle, wetting, and spreading	11	3.3.1 Adsorption and the dividing surface	35
2.4 The surface of tension	14	3.3.2 Conventions for the dividing surface	36
2.5 Work of adhesion and cohesion	14	3.3.3 Adsorption isotherms	37
2.6 Measurement of surface tension	15	3.4 Thermodynamic properties of interfaces	38
2.6.1 Wilhelmy plate	15	3.4.1 Mechanical work	38
		3.4.2 Internal energy and enthalpy	38
		3.4.3 Gibbs free energy	39

3.5 Surface excess quantities	39	4.7.5 Factors affecting the cmc	64
3.6 Measurement of adsorption	40	4.7.6 Impurity effects	66
3.6.1 Adsorption from concentration change	40	4.8 Applications of surfactants	67
3.6.2 Adsorption from surface analysis	41	4.8.1 Wetting	67
3.6.3 Adsorption from surface tension change – the Gibbs adsorption isotherm	41	4.8.2 Detergency	68
3.7 Adsorption from solutions	42	4.8.3 Water repulsion	70
SUMMARY	43	4.8.4 Emulsification	70
FURTHER READING	43	4.8.5 Froth flotation in ore treatment	70
EXERCISES	43	4.8.6 Oil recovery	71
		4.8.7 Membrane disruption	71
		4.9 Films and foams	72
Chapter 4		4.9.1 Introduction	72
Adsorption at the gas–liquid interface	45	4.9.2 Film tension	73
4.1 Introduction	46	4.9.3 Permeability to gases	73
4.2 Measurement of equilibrium adsorption	46	4.9.4 Foam formation	74
4.2.1 Surface tension measurement	46	4.9.5 The Plateau border	75
4.2.2 Surface analysis	47	4.10 The Marangoni effect	75
4.3 Observation of adsorption kinetics	47	4.11 Aerosols	77
4.3.1 Adsorption at freshly formed interfaces	48	4.11.1 Occurrence	77
4.3.2 Surface waves	49	4.11.2 Formation	77
4.4 Adsorption of non-electrolyte solutes	50	4.11.3 Monodisperse aerosols	78
4.4.1 Effects of solute concentration on the surface tension	50	4.11.4 Electrostatic precipitation	78
4.4.2 Szyszkowski–Langmuir adsorption	51	4.11.5 Verification of the Kelvin equation	78
4.4.3 Equations of state	53	SUMMARY	79
4.4.4 Negative adsorption	54	FURTHER READING	79
4.4.5 Kinetics of adsorption	54	REFERENCES	80
4.5 Adsorption of ionized solutes	55	EXERCISES	81
4.6 Adsorption of surfactants	56	Chapter 5	
4.6.1 Molecular structure of surfactants	56	Insoluble monolayers and Langmuir–Blodgett films	83
4.6.2 The surface tension of surfactant solutions	57	5.1 Introduction	84
4.6.3 Adsorption of surfactants	57	5.2 Formation and handling of floating monolayers	85
4.7 Micelles	60	5.2.1 Molecular requirements	85
4.7.1 Molecular requirements	61	5.2.2 Spreading	85
4.7.2 Formation of micelles	61	5.2.3 The surface film balance	86
4.7.3 Micelle structure	63	5.2.4 The Brooks frame	87
4.7.4 Solubilization	63	5.3 Surface pressure–area relationships	87

5.4 Deposition of Langmuir-Blodgett films	88	6.2.3 Size distribution	122
5.5 The study of film structure	90	6.2.4 Emulsion stability	123
5.5.1 The surface film balance	90	6.2.5 Emulsion rheology	126
5.5.2 Surface potential	90	6.3 Emulsion stability and selection of the emulsifier	128
5.5.3 Surface viscosity	91	6.3.1 Early theories	128
5.5.4 X-ray scattering techniques	92	6.3.2 Electrical aspects of emulsion stability	129
5.5.5 Neutron scattering	94	6.3.3 Steric stabilization	130
5.5.6 Vibrational and electronic spectroscopy	94	6.3.4 Stabilization by solid particles	132
5.5.7 Electron diffraction	95	6.3.5 Emulsifiers and the HLB system	132
5.5.8 Electron microscopy	95	6.4 Microemulsions	133
5.5.9 Ellipsometry	96	6.5 Emulsion polymerization	135
5.5.10 Brewster angle and fluorescence microscopy	96	6.6 Liquid-liquid extraction	137
5.5.11 Scanning probe microscopy	97	6.7 Membranes	137
5.5.12 Surface plasmon resonance	97	6.7.1 Artificial membranes	138
5.5.13 Miscellaneous techniques for solid surfaces	98	6.7.2 Black lipid membranes (BLMs)	142
5.6 The structure and properties of monolayers	98	6.7.3 Self-assembled membranes	142
5.6.1 The principal monolayer phases	98	SUMMARY	144
5.6.2 Phase transitions	101	FURTHER READING	144
5.6.3 Equilibrium spreading pressure	103	REFERENCES	145
5.6.4 Monolayer collapse	103	EXERCISES	145
5.7 Interactions in monolayers	104	Chapter 7	
5.7.1 Two water-insoluble components	104	The surfaces of solids	146
5.7.2 Penetration of monolayers by soluble surfactants	107	7.1 Introduction	146
5.7.3 Reactions in monolayers	108	7.2 Surfaces of single crystals	147
5.8 The structure of LB films	109	7.3 Techniques for studying solid surfaces	148
5.9 Applications	111	7.3.1 Spectroscopic and diffraction methods	148
5.9.1 Spread monolayers	111	7.3.2 Scanning probe techniques	157
5.9.2 LB films	112	SUMMARY	160
SUMMARY	115	FURTHER READING	160
FURTHER READING	115	REFERENCES	160
REFERENCES	116	EXERCISES	161
EXERCISES	117	Chapter 8	
Chapter 6		Adsorption at the gas-solid interface	163
The liquid-liquid interface; membranes	119	8.1 Introduction	163
6.1 Introduction	119	8.2 Physical and chemical adsorption	164
6.2 Emulsions	120	8.2.1 Contrasts between physical and chemical adsorption	164
6.2.1 The formation of emulsions	121		
6.2.2 Emulsion type	122		

8.3 Measurement of gas adsorption	165	9.7 Colloidal dispersions	199
8.3.1 Volumetric methods	165	9.7.1 Lyophilic and lyophobic colloids	199
8.3.2 Flow methods	166	9.7.2 Preparation of colloids	200
8.3.3 Gravimetric methods	167	9.8 The properties of colloids	201
8.4 Adsorption isotherms	167	9.8.1 Brownian motion	201
8.4.1 Introduction	167	9.8.2 Light scattering	201
8.4.2 Classification of adsorption isotherms	168	9.8.3 Measurement of particle size	203
8.5 Isotherm equations	168	9.8.4 Measurement of particle charge	204
8.5.1 The Langmuir adsorption equation	170	9.9 Coagulation of lyophobic colloids by electrolytes	206
8.5.2 The BET equation	172	9.9.1 Surface charge	206
8.5.3 The BET equation for limited adsorption	176	9.9.2 The Schulze–Hardy rule	206
8.5.4 The Freundlich and Temkin isotherms	176	9.9.3 Stability of colloidal dispersions – DLVO theory	207
8.5.5 Other isotherm equations	177	9.9.4 Kinetics of coagulation	211
8.6 Capillary condensation	177	9.9.5 Limitations of DLVO theory	212
8.7 Chemisorption	179	9.9.6 The measurement of interparticle forces	212
8.7.1 Adsorption isotherms	179	9.10 Solvation effects in colloid interactions	213
8.8 Heterogeneous catalysis	180	9.10.1 Solvent structuring in particle interactions	213
8.8.1 Mechanisms of heterogeneous catalysis	181	9.10.2 Steric stabilization of colloids	215
SUMMARY	185	9.11 Self-assembled films	215
FURTHER READING	185	SUMMARY	218
REFERENCES	185	FURTHER READING	218
EXERCISES	186	REFERENCES	219
		EXERCISES	219
Chapter 9		Chapter 10	
The liquid–solid interface; colloids	188	Biological interfaces	221
9.1 Introduction	188	10.1 Introduction	221
9.2 Measurement	189	10.2 Membrane materials	222
9.3 Adsorption at low solute concentration	189	10.2.1 Phospholipids	222
9.4 Adsorption at higher solute concentrations	192	10.2.2 Cholesterol	225
9.4.1 Composite adsorption isotherm	192	10.2.3 Phospholipid + cholesterol	225
9.5 Adsorption of ions and the electrical double layer	194	10.2.4 Membrane proteins	225
9.5.1 Helmholtz model	194	10.3 Bilayers	226
9.5.2 Gouy–Chapman model	195	10.3.1 Structure	226
9.5.3 The Stern model	197	10.3.2 Properties	228
9.6 Electrokinetics	198	10.4 Vesicles and liposomes	229
		10.4.1 Phospholipid self-assembly	229

10.4.2 Electron microscopy	231	10.6.1 Natural lung surfactant: composition and function	239
10.4.3 Applications	231	10.6.2 Lung surfactant production and life cycle	239
10.5 Cell membranes	232	10.6.3 Lung surfactant surface activity	240
10.5.1 Composition	232	SUMMARY	240
10.5.2 Structure	232	FURTHER READING	241
10.5.3 Function: selective permeability	234	REFERENCES	242
10.5.4 Surfactant effects	237	Index	243
10.5.5 Molecular recognition	238		
10.6 Lung surfactant	238		