# Contents

Preface

Useful Constants

Symbols and Some Basic Abbreviations

About the Companion Web Site

## 1 Introduction to Colloid and Surface Chemistry

1.1 What are the colloids and interfaces? Why are they important? Why do we study them together?

1.1.1 Colloids and interfaces

1.2 Applications

1.3 Three ways of classifying the colloids

1.4 How to prepare colloid systems

1.5 Key properties of colloids

1.6 Concluding remarks

Appendix 1.1

Problems

References

## 2 Intermolecular and Interparticle Forces

2.1 Introduction – Why and which forces are of importance in colloid and surface chemistry?

2.2 Two important long-range forces between molecules

2.3 The van der Waals forces

2.3.1 Van der Waals forces between molecules

2.3.2 Forces between particles and surfaces

2.3.3 Importance of the van der Waals forces

2.4 Concluding remarks

Appendix 2.1 A note on the uniqueness of the water molecule and some of the recent debates on water structure and peculiar properties

References for the Appendix 2.1

Problems

References
3 Surface and Interfacial Tensions – Principles and Estimation Methods 34
  3.1 Introduction 34
  3.2 Concept of surface tension – applications 34
  3.3 Interfacial tensions, work of adhesion and spreading 39
    3.3.1 Interfacial tensions 39
    3.3.2 Work of adhesion and cohesion 43
    3.3.3 Spreading coefficient in liquid–liquid interfaces 44
  3.4 Measurement and estimation methods for surface tensions 45
    3.4.1 The parachor method 46
    3.4.2 Other methods 48
  3.5 Measurement and estimation methods for interfacial tensions 50
    3.5.1 “Direct” theories (Girifalco–Good and Neumann) 51
    3.5.2 Early “surface component” theories (Fowkes, Owens–Wendt, Hansen/Skaarup) 52
    3.5.3 Acid–base theory of van Oss–Good (van Oss et al., 1987) – possibly the best theory to-date 57
    3.5.4 Discussion 59
  3.6 Summary 60
Appendix 3.1 Hansen solubility parameters (HSP) for selected solvents 61
Appendix 3.2 The “φ” parameter of the Girifalco–Good equation (Equation 3.16) for liquid–liquid interfaces. Data from Girifalco and Good (1957, 1960) 66
Problems 67
References 72

4 Fundamental Equations in Colloid and Surface Science 74
  4.1 Introduction 74
  4.2 The Young equation of contact angle 74
    4.2.1 Contact angle, spreading pressure and work of adhesion for solid–liquid interfaces 74
    4.2.2 Validity of the Young equation 77
    4.2.3 Complexity of solid surfaces and effects on contact angle 78
  4.3 Young–Laplace equation for the pressure difference across a curved surface 79
  4.4 Kelvin equation for the vapour pressure, $P$, of a droplet (curved surface) over the “ordinary” vapour pressure $P_{\text{sat}}$ for a flat surface 80
    4.4.1 Applications of the Kelvin equation 81
  4.5 The Gibbs adsorption equation 82
  4.6 Applications of the Gibbs equation (adsorption, monolayers, molecular weight of proteins) 83
  4.7 Monolayers 86
  4.8 Conclusions 89
Appendix 4.1 Derivation of the Young–Laplace equation 90
Appendix 4.2 Derivation of the Kelvin equation 91
Appendix 4.3 Derivation of the Gibbs adsorption equation 91
Problems 93
References 95

5 Surfactants and Self-assembly. Detergents and Cleaning 96
  5.1 Introduction to surfactants – basic properties, self-assembly and critical packing parameter (CPP) 96
  5.2 Micelles and critical micelle concentration (CMC) 99
8.3 Sedimentation and creaming (Stokes and Einstein equations) 187
  8.3.1 Stokes equation 187
  8.3.2 Effect of particle shape 188
  8.3.3 Einstein equation 190
8.4 Kinetic properties via the ultracentrifuge 191
  8.4.1 Molecular weight estimated from kinetic experiments (1 = medium and
       2 = particle or droplet) 193
  8.4.2 Sedimentation velocity experiments (1 = medium and 2 = particle or droplet) 193
8.5 Osmosis and osmotic pressure 193
8.6 Rheology of colloidal dispersions 194
  8.6.1 Introduction 194
  8.6.2 Special characteristics of colloid dispersions’ rheology 196
8.7 Concluding remarks 198
Problems 198
References 201

9 Characterization Methods of Colloids – Part II: Optical Properties (Scattering,
Spectroscopy and Microscopy) 202
  9.1 Introduction 202
  9.2 Optical microscopy 202
  9.3 Electron microscopy 204
  9.4 Atomic force microscopy 206
  9.5 Light scattering 207
  9.6 Spectroscopy 209
  9.7 Concluding remarks 210
Problems 210
References 210

10 Colloid Stability – Part I: The Major Players (van der Waals and Electrical Forces) 211
  10.1 Introduction – key forces and potential energy plots – overview 211
       10.1.1 Critical coagulation concentration 213
  10.2 van der Waals forces between particles and surfaces – basics 214
  10.3 Estimation of effective Hamaker constants 215
  10.4 vdW forces for different geometries – some examples 217
       10.4.1 Complex fluids 219
  10.5 Electrostatic forces: the electric double layer and the origin of surface charge 219
  10.6 Electrical forces: key parameters (Debye length and zeta potential) 222
       10.6.1 Surface or zeta potential and electrophoretic experiments 223
       10.6.2 The Debye length 225
  10.7 Electrical forces 228
       10.7.1 Effect of particle concentration in a dispersion 229
  10.8 Schulze–Hardy rule and the critical coagulation concentration (CCC) 230
  10.9 Concluding remarks on colloid stability, the vdW and electric forces 233
       10.9.1 vdW forces 233
       10.9.2 Electric forces 234
Appendix 10.1 A note on the terminology of colloid stability 235
### 11 Colloid Stability – Part II: The DLVO Theory – Kinetics of Aggregation

11.1 DLVO theory – a rapid overview
11.2 DLVO theory – effect of various parameters
11.3 DLVO theory – experimental verification and applications
  11.3.1 Critical coagulation concentration and the Hofmeister series
  11.3.2 DLVO, experiments and limitations
11.4 Kinetics of aggregation
  11.4.1 General – the Smoluchowski model
  11.4.2 Fast (diffusion-controlled) coagulation
  11.4.3 Stability ratio W
  11.4.4 Structure of aggregates
11.5 Concluding remarks
Problems
References

### 12 Emulsions

12.1 Introduction
12.2 Applications and characterization of emulsions
12.3 Destabilization of emulsions
12.4 Emulsion stability
12.5 Quantitative representation of the steric stabilization
  12.5.1 Temperature-dependency of steric stabilization
  12.5.2 Conditions for good stabilization
12.6 Emulsion design
12.7 PIT – Phase inversion temperature of emulsion based on non-ionic emulsifiers
12.8 Concluding remarks
Problems
References

### 13 Foams

13.1 Introduction
13.2 Applications of foams
13.3 Characterization of foams
13.4 Preparation of foams
13.5 Measurements of foam stability
13.6 Destabilization of foams
  13.6.1 Gas diffusion
  13.6.2 Film (lamella) rupture
  13.6.3 Drainage of foam by gravity
13.7 Stabilization of foams
  13.7.1 Changing surface viscosity
  13.7.2 Surface elasticity
13.7.3 Polymers and foam stabilization 295
13.7.4 Additives 296
13.7.5 Foams and DLVO theory 296
13.8 How to avoid and destroy foams 296
13.8.1 Mechanisms of antifoaming/defoaming 297
13.9 Rheology of foams 299
13.10 Concluding remarks 300
Problems 301
References 302

14 Multicomponent Adsorption 303
14.1 Introduction 303
14.2 Langmuir theory for multicomponent adsorption 304
14.3 Thermodynamic (ideal and real) adsorbed solution theories (IAST and RAST) 306
14.4 Multicomponent potential theory of adsorption (MPTA) 312
14.5 Discussion. Comparison of models 315
14.5.1 IAST – literature studies 315
14.5.2 IAST versus Langmuir 315
14.5.3 MPTA versus IAST versus Langmuir 317
14.6 Conclusions 317
Acknowledgments 319
Appendix 14.1 Proof of Equations 14.10a,b 319
Problems 319
References 320

15 Sixty Years with Theories for Interfacial Tension – Quo Vadis? 321
15.1 Introduction 321
15.2 Early theories 321
15.3 van Oss–Good and Neumann theories 331
15.3.1 The two theories in brief 331
15.3.2 What do van Oss–Good and Neumann say about their own theories? 333
15.3.3 What do van Oss–Good and Neumann say about each other’s theories? 334
15.3.4 What do others say about van Oss–Good and Neumann theories? 335
15.3.5 What do we believe about the van Oss–Good and Neumann theories? 338
15.4 A new theory for estimating interfacial tension using the partial solvation parameters (Panayiotou) 339
15.5 Conclusions – Quo Vadis? 344
Problems 345
References 349

16 Epilogue and Review Problems 352
Review Problems in Colloid and Surface Chemistry 353

Index 358