Contents

Preface XIII

1	General introduction 1				
	References 6				
2	Interparticle Interactions and Their Combination 7				
2.1	Hard-Sphere Interaction 7				
2.2	"Soft" or Electrostatic Interaction 7				
2.3	Steric Interaction 10				
2.4	van der Waals Attractions 14				
2.5	Combination of Interaction Forces 16				
2.6	Flocculation of Dispersions, and Its Prevention 18				
2.6.1	Mechanism of Flocculation 19				
2.6.1.1	Flocculation of Electrostatically Stabilized Suspensions 19				
2.6.1.2					
2.6.1.3	Bridging or Charge Neutralization by Polymers 23				
2.6.2	General Rules for Reducing (Eliminating) Flocculation 23				
2.7	Distinction between "Dilute," "Concentrated," and "Solid"				
	Dispersions 24				
2.8	States of Suspension on Standing 27				
2.9	States of the Emulsion on Standing 29				
2.9.1	Creaming and Sedimentation 30				
2.9.2	Flocculation 31				
2.9.3	Ostwald Ripening (Disproportionation) 32				
2.9.4	Emulsion Coalescence 34				
2.9.5	Phase Inversion 35				
	References 36				
3	Principles of Steady-State Measurements 37				
3.1	Strain Rate or Shear Rate 38				
3.2	Types of Rheological Behavior in Simple Shear 38				
3.2.1	Models for Flow Behavior 39				

Rheology of Dispersions: Principles and Applications. Tharwat F. Tadros $\ \, \otimes$ 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 978-3-527-32003-5

VIII	Contents	
·	3.2.1.1	Law of Elasticity (Hooke's Model) 39
	3.2.1.2	Newton's Law of Viscosity 39
	3.2.1.3	The Kinematic Viscosity v 40
	3.2.1.4	Non-Newtonian Flow 40
	3.2.2	Rheological Models for the Analysis of Flow Curves 41
		Newtonian Systems 41
	3.2.2.2	Bingham Plastic Systems 41
	3.2.2.3	1 (8/ /
	3.2.2.4	Dilatant (Shear Thickening) System 43
	3.2.2.5	The Herschel–Bulkley General Model 43
	3.2.2.6	The Casson Model 44
	3.2.2.7	1
	3.3	Time Effects During Flow: Thixotropy and Negative (or Anti-)
		Thixotropy 46
	3.4	Rheopexy 48
	3.5	Turbulent Flow 50
	3.6	Effect of Temperature 52
	3.7	Measurement of Viscosity as a Function of Shear Rate: The Steady-
		State Regime 53
	3.7.1	Capillary Viscometers 54
	3.7.2	Measurement of Intrinsic Viscosity of Polymers 55
	3.7.3	Capillary Rheometry for Non-Newtonians 56
	3.7.4	Rotational Viscometers 57
	3.7.4.1	Concentric Cylinder Viscometer 57
	3.8	Non-Newtonians 58
	3.8.1	Shear Thinning or Pseudoplastic 58
	3.8.2	Bingham Plastic 59
	3.9	Major Precautions with Concentric Cylinder Viscometers 59
	3.9.1	Shear Rate Calculations 59 Wall Slip and Sample Evaporation During Measurement 60
	3.9.2 3.9.2.1	
	3.9.2.1	
	3.9.2.3	Parallel Plates (Discs) 62 The Brookfield Viscometer 62
	3.3.4.4	References 64
		ICICICIACS UT

4 Principles of Viscoelastic Behavior 654.1 Introduction 65

- 4.2 The Deborah Number 65
- 4.3 Strain Relaxation after the Sudden Application of Stress (Creep) 66
- 4.4 Analysis of Creep Curves 67
- 4.4.1 Viscous Fluid 674.4.2 Elastic Solid 67
- 4.4.3 Viscoelastic Response 68
- 4.4.3.1 Viscoelastic Liquid 68
- 4.4.3.2 Viscoelastic Solid 69

4.5	The Berger Model (Maxwell + Kelvin) 70			
4.6	Creep Procedure 71			
4.7	Stress Relaxation after Sudden Application of Strain 72			
4.8	Dynamic (Oscillatory) Techniques 74			
4.8.1	Analysis of Oscillatory Response for a Viscoelastic System 74			
4.8.1.1	Vector Analysis of the Complex Modulus 76			
4.8.1.2	The Cohesive Energy Density E_c 78			
4.8.1.3	The Weissenberg Effect and Normal Forces 79			
4.8.2	Viscoelastic Measurements 79			
4.8.2.1	Constant Stress (Creep) Measurements 80			
4.8.2.2	Dynamic (Oscillatory) Measurements 82			
4.8.2.3	Shear Modulus (Rigidity) Measurement 83			
	References 84			
5	Rheology of Suspensions 85			
5.1	Introduction 85			
5.2	The Einstein Equation 86			
5.3	The Bachelor Equation 86			
5.4	Rheology of Concentrated Suspensions 86			
5.5	Rheology of Hard-Sphere Suspensions 87			
5.5.1	,			
5.6	Rheology of Systems with "Soft" or Electrostatic Interaction 89			
5.6.1	, 1			
5.6.1.1	Elastic Modulus (G')–Distance (h) Relation 92			
5.6.1.2	Scaling Laws for Dependence of G' on ϕ 93			
5.6.2	Control of Rheology of Electrostatically Stabilized Suspensions 94			
5.7	Rheology of Sterically Stabilized Dispersions 94			
5.7.1	Viscoelastic Properties of Sterically Stabilized Suspensions 95			
5.7.2	Correlation of the Viscoelastic Properties of Sterically Stabilized			
	Suspensions with Their Interparticle Interactions 96			
5.7.3	The High-Frequency Modulus–Volume Fraction Results 98			
5.8	Rheology of Flocculated Suspensions 99			
5.8.1	Weakly Flocculated Suspensions 100			
5.8.2	Strongly Flocculated (Coagulated) Suspensions 106			
5.8.2.1	Analysis of the Flow Curve 107			
5.8.2.2	1			
5.8.2.3	Examples of Strongly Flocculated (Coagulated) Suspensions 109			
5.8.2.4	Strongly Flocculated, Sterically Stabilized Systems 111			
5.9	Models for the Interpretation of Rheological Results 116			
5.9.1	Doublet Floc Structure Model 116			
5.9.2	Elastic Floc Model 117			
	References 118			
6	Rheology of Emulsions 121			
6.1	Introduction 121			
6.2	Interfacial Rheology 121			

ĸ	Contents				
	6.2.1	Interfacial Tension and Surface Pressure 121			
	6.2.2	Interfacial Shear Viscosity 122			
	6.2.2.1	Measurement of Interfacial Viscosity 122			
	6.2.3	Interfacial Dilational Elasticity 123			
	6.2.4	Interfacial Dilational Viscosity 124			
	6.2.5	Non-Newtonian Effects 124			
	6.2.6	Correlation of Emulsion Stability with Interfacial Rheology 124			
	Mixed-Surfactant Films 124				
6.2.6.2 Protein Films 124					
6.3 Bulk Rheology of Emulsions 126					
	6.3.1	Analysis of the Rheological Behavior of Concentrated Emulsions 128			
	6.3.1.1	Experimental $\eta_r - \phi$ Curves 131			
	6.3.1.2	Influence of Droplet Deformability 131			
	6.3.2	Viscoelastic Properties of Concentrated Emulsions 132			
	6.3.2.1	High-Internal Phase Emulsions (HIPES) 133			
	6.3.2.2	Deformation and Break-Up of Droplets in Emulsions During Flow 138			
		References 146			
	7	Rheology Modifiers, Thickeners, and Gels 149			
	7.1	Introduction 149			
	7.2	Classification of Thickeners and Gels 149			
	7.3	Definition of a "Gel" 150			
	7.4	Rheological Behavior of a "Gel" 150			
	7.4.1	Stress Relaxation (after Sudden Application of Strain) 150			
	7.4.2	Constant Stress (Creep) Measurements 151			
	7.4.3	Dynamic (Oscillatory) Measurements 152			
	7.5	Classification of Gels 153			
	7.5.1	Polymer Gels 154			
	7.5.1.1	Physical Gels Obtained by Chain Overlap 154			
	7.5.1.2	Gels Produced by Associative Thickeners 155			
	7.5.1.3	Crosslinked Gels (Chemical Gels) 159			
	7.5.2	Particulate Gels 160			
	7.5.2.1	Aqueous Clay Gels 160			
	7.5.2.2 7.5.2.3	Organo-Clays (Bentones) 161 Oxide Gels 162			
	7.5.2.3	Gels Produced using Particulate Solids and High-Molecular-Weight			
	7.3.2.4	Polymers 163			
	7.6	Rheology Modifiers Based on Surfactant Systems 164			
	7.0	References 167			
	8	Use of Rheological Measurements for Assessment and Prediction of the			
	3	Long-Term Physical Stability of Formulations (Creaming and			
		Sedimentation) 169			
	8.1	Introduction 169			
	8.2	Sedimentation of Suspensions 169			
	J				

8.2.2	Application of a High-Gravity (g) Force 172		
8.2.3	Rheological Techniques for the Prediction of Sedimentation or		
	Creaming 173		
8.2.4	Separation of Formulation: Syneresis 174		
8.2.5	Examples of Correlation of Sedimentation or Creaming with Residual		
(Zero-Shear) Viscosity 175			
8.2.5.1	Model Suspensions of Aqueous Polystyrene Latex 175		
8.2.5.2	Sedimentation in Non-Newtonian Liquids 175		
8.2.5.3	Role of Thickeners 176		
8.2.6	Prediction of Emulsion Creaming 177		
8.2.6.1	Creep Measurements for Prediction of Creaming 179		
8.2.6.2	Oscillatory Measurements for Prediction of Creaming 179		
8.3	Assessment and Prediction of Flocculation Using Rheological		
	Techniques 180		
8.3.1	Introduction 180		
8.3.2	Wall Slip 180		
8.3.3	<u> </u>		
8.3.4	Influence of Ostwald Ripening and Coalescence 181		
8.3.5	Constant-Stress (Creep) Experiments 181		
8.3.6	Dynamic (Oscillatory) Measurements 182		
8.3.6.1	Strain Sweep Measurements 182		
8.3.6.2	Oscillatory Sweep Measurements 183		
8.3.7 Examples of Application of Rheology for Assessment and Prediction			
	Flocculation 184		
8.3.7.1	Flocculation and Restabilization of Clays Using Cationic		
	Surfactants 184		
8.3.7.2	Flocculation of Sterically Stabilized Dispersions 185		
8.3.7.3	Flocculation of Sterically Stabilized Emulsions 186		
8.4 Assessment and Prediction of Emulsion Coalescence Using			
	Rheological Techniques 187		
8.4.1	Introduction 187		
8.4.2	Rate of Coalescence 187		
8.4.3	Rheological Techniques 188		
8.4.3.1	Viscosity Measurements 188		
8.4.3.2	Measurement of Yield Value as a Function of Time 189		
8.4.3.3	Measurement of Storage Modulus G' as a Function of Time 189		
8.4.4	Correlation between Elastic Modulus and Coalescence 190		
8.4.5	Cohesive Energy $E_{\rm c}$ 191		
	References 191		

Accelerated Tests and Their Limitations 171

8.2.1