ABSTRACT

A method was developed to determine the particle size distribution of colloidal particles suspended in a fluid based on light transmittance measurements at various wavelengths. This method requires that the nature of the particle size distribution be assumed a priori.

A technique to determine the orthokinetic coalescence efficiency of polydisperse emulsion droplets in simple shear flow was developed. The technique is based on comparing results of experimentally measured and theoretically calculated light transmittance intensities. The orthokinetic coalescence efficiency was assumed to be a function of the colliding droplets radius ratio and their surface potential which determines the maximum radius above which the orthokinetic coalescence efficiency is zero.

The effects of electrolytes, surface active agents, presence of solid particles at the water/oil interface, interfacial tension and shear rate on the orthokinetic coalescence efficiency were studied.

The coalescence process was mathematically simulated using a Monte Carlo method. The change in droplet size distribution as the number of collisions between the emulsion droplets proceeds was calculated. The self-preserving form hypothesis was tested. It was found that the distributions studied were all of this form.

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RESUME

Une méthode a été développée pour déterminer la répartition de diamètres de particules d'une suspension colloïdale dans un milieu liquide, en mesurant la transmittance émise à différentes longueurs d'ondes. Cette méthode nécessite qu'un type de répartition ou de distribution soit supposé au départ.

Une méthode fut développée afin de déterminer l'efficacité des collisions orthocinétiques d'une émulsion polydisperse dans un flux de cisaillement simple. Cette technique s'appuie sur la comparaison de résultats expérimentaux avec ceux calculés théoriquement à partir de l'intensité de la lumière transmise. Comme hypothèse de départ, l'efficacité de la coalescence orthocinétique fut supposée varier en fonction du rapport des rayons des gouttes entrant en collision, ainsi que de leur potentiel de surface, définissant le rayon maximum au-desses duquel l'efficacité de la collision orthocinétique est nulle.

L'influence d'électrolytes, d'agents surfactants, de la présence de particules solides à l'interface eau/huile, de la tension de surface, ainsi que de la vitesse de cisaillement fut étudiée.

Une simulation mathématique du procédé de coalescence fut obtenu à l'aide de la méthode de Monte Carlo. Des modifications de la répartition du diamètre des gouttes furent calculées selon le nombre de collisions s'effectuant entre les gouttes de l'émulsion.

L'hypothèse de la "self-preserving form", où un type initial de répartition est conservé, fut testée. Les résultats indiquent que les répartitions étudiées furent toutes de ce type.

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TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

GENERAL REMARKS				
The Orthokinetic Collision Efficiency	4			
Orthokinetic Collision Efficiency in Various Shear Flows	10			
Flow in a tube	10			
Flow between two coaxial cylinders	13			
Smoluchowski's Coagulation Equation for Polydisperse Systems .	14			
Ultrasonic Emulsification	15			
REFERENCES	20			
NOMENCLATURE				

CHAPTER 2

TURBIDIMETRIC DETERMINATION OF PARTICLE SIZE DISTRIBUTIONS	
ABSTRACT	26
INTRODUCTION	27
THEORY	29
Procedure I	31
Procedure II	34
Particle Size Distributions	34
EXPERIMENTAL PART	36
RESULTS AND DISCUSSION	38
COMPARISON WITH OTHER TURBIDIMETRIC METHODS	46
CONCLUDING REMARKS	47

	Page
REFERENCES	49
NOMENCLATURE	51
APPENDIX 2-A	
Mathematical Representation of Q in Terms of Spherical Bessel Functions of order (n + $1/2$)	53
APPENDIX 2-B	
A Listing of the Fortran Subroutine MISCAT which was Used to Calculate the Scattering Efficiency of Dispersed Colloidal Particles	66
APPENDIX 2-C	
Mathematic Derivation of n_1^* as a Function of \overline{a} and σ for a Gaussian and a Gamma Distribution Function	69

.

CHAPTER 3

\$

STABILITY OF WATER IN OIL EMULSIONS IN SIMPLE SHEAR FLOW				
1. DETERMINATION OF THE ORTHOKINETIC COALESCENCE EFFICIENCY				
ABSTRACT	73			
INTRODUCTION	74			
THEORETICAL ANALYSIS	77			
A METHOD FOR ESTIMATING THE ORTHOKINETIC COALESCENCE EFFICIENCY				
EXPERIMENTAL DETAILS				
Experimental Apparatus	88			
Material	94			
Cleaning of the Glassware	94			
RESULTS AND DISCUSSION	95			
Effect of a on α	105			
Effect of the Value of C on α_{c}	107			
•				

CONCLUDING REMARKS 1	09			
REFERENCES				
NOMENCLATURE 1	14			
APPENDIX 3-A				
A Listing of the Fortran Subroutine Coalesce that Integrates Shear Induced Smoluchowski's Coalescence Equation	.17			
APPENDIX 3-B				
Mathematical Derivation Which Illustrates the Estimation of α_{c} at t = 0	.24			
APPENDIX 3-C				
Photograph of Microcouette Apparatus Used to Induce Shear Coalescence, the Laser Light Source, Speed Motor, Glass Plates, Photodiode, Data Acquisition System and Computer can be Seen 1	26			
APPENDIX 3-D				
Solution of the Continuity Equation and the Navier-Stokes Equation for Flow in the Microcouette Apparatus	27			
CHAPTER 4				
STABILITY OF WATER IN OIL EMULSIONS IN SIMPLE SHEAR FLOW				
2. THE EFFECTS OF ADDITIVES ON THE ORTHOKINETIC COALESCENCE EFFICIENCY	Y			
ABSTRACT	33			
INTRODUCTION 1	33			
EXPERIMENTAL DETAILS	133			
Experimental Apparatus1	34			
Preparation of the Emulsion1	35			

Page

136

RESULTS AND DISCUSSION Effect of the Shear Rate on α_{c} 144 Effect of the Presence of KCl, AlCl₃ and SDS on α_c 150

Effect of the Concentration of KCl on α_{c}	157
Effect of the Interfacial Tension on α_{c}	159
Effect of the Presence of Solid Particles on α_{c}	162
CONCLUDING REMARKS	166
REFERENCES	168
NOMENCLATURE	170

Page

CHAPTER 5

SHEAR INDUCED COALESCENCE OF WATER IN OIL EMULSION DROPLETS

SIMULATED BY A MONTE CARLO METHOD

ABSTRACT	173
INTRODUCTION	174
THEORETICAL ANALYSIS	176
Generation of a Random Droplet	181
RESULTS AND DISCUSSION	184
SELF-PRESERVING FORM DISTRIBUTIONS	193
CONCLUSIONS	197
REFERENCES	198
NOMENCLATURE	200
APPENDIX 5-A	

The Subroutine MOCARLO that Simulates the Shear Induced Coalescence of Emulsion Droplets by a Monte Carlo Method 201

CHAPTER 6

GENERAL CONCLUSIONS

C

CLAIMS FOR ORIGINAL RESEARCH	209
RECOMMENDATIONS FOR FUTURE WORK	210
REFERENCES	212

.

Page

LIST OF FIGURES

C

CHAPTER 1

Page

Fig.	1	The collision process between two droplets approaching	
		each other in simple shear flow is shown.	
		(a) If the center of sphere a does not pass through the	
		collision sphere shown by a sphere of radius a + a then	
		no collision occurs. If sphere a passes through the	
		collision sphere then a collision occurs.	
		(b) If sphere a, is captured by the central sphere then	
		the collision is termed successful and leads to coales-	
		cence.	
		(c) If sphere a collides with the central sphere and	
		is still not captured, then the collision is termed	
		unsuccessful and no coalescence occurs	3
Fig.	2	A central sphere of radius a, and a collision sphere	
		of radius a + a are shown. The center of both spheres	
		is the center of a Cartesian coordinate system. A sphere	
		of radius a approaching a from ∞ in simple shear flow	
		is also shown. If a passes through the quadrant shown	
		in the figure, then it will collide with the central	
		sphere	5
Fig.	3	The dependence of α_{α} on the dimensionless number C where	
		the dimensionless number C_{p} is a parameter is qualita-	
		tively shown. In the absence of repulsion forces (C_{R} =	
		0), α increases as C increases. In the presence of	
		repulsive forces ($C_{R} > 0$) α versus log (C_{A}^{-1}) goes	
		through a minimum and maximum consecutively	9
Fig.	4	The trajectories of a sphere a approaching another	
		sphere a in simple shear flow is shown. These tra-	
		jectories can be divided into open trajectories and	
		closed trajectories. The two types of trajectories are	
		separated by a limiting trajectory. The minimum dis-	
		tance, d , a can approach a is also shown	11

		Page
Fig. 5	The process of forming a droplet by applying ultra-	
	sonic waves at the interface between two immiscible	
	liquids is depicted.	
	(a) The two phases before the application of the	
	ultrasonic waves.	
	(b) Mass of liquid I penetrates liquid II upon the	
	application of ultrasonic waves.	
	(c) Formation of a large droplet followed by a small	

CHAPTER 2

sattelite droplet

18

Fig.	1	Calculated values of the scattering efficiency versus	
		the dimensionless variable X for various values of the	
		refractive index ratio m	32
Fig.	2	Schematic diagram of the experimental apparatus. L -	
		light source. S - sample holder surrounded by a jacket	
		of flowing water. T - temperature control bath. CU -	
		cuvette with sample or reference material. G - grating.	
		D - photodiode-array. C - computer. P - plotter	37
Fig.	3	Experimentally observed change of $I_{\downarrow}/I_{\downarrow}$ with wavelength	
		for water/silicone oil emulsion, monodisperse latex	
		dispersion and bimodal latex dispersionn	39
Fig.	4	Comparison between the experimental and theoretical	
		values of (I_t/I_p) for the bimodal latex dispersion and	
		the water/silicone oil emulsion. In the figure the	
		solid lines and the symbols represent the theoretical	
		and experimental values, respectively	43

CHAPTER 3

vii

Fig. 1	Trajectories of two spheres of radii a_1 and a_2 in simple
	shear flow. The central particle is located at the
	center of a Cartesian coordinate system. The flow is
	characterized by open trajectories and closed trajec-
	tories, separated by limiting trajectories. In the

	absence of colloidal forces between the particles, the	
	minimum distance d, particle a_ can approach a_ is	
	defined as the minimum distance between a particle on	
	a limiting trajectory in the equatorial plane and the	
	reference particle	81
Fig. 2	The dependence of α / α on q_{1} for different values of	
	the constant C as given by Eqs. (11)	83
Fig. 3	Illustration of the method used to estimate the ortho-	
	kinetic collision efficiency. At any time t*, the	
	value of T at which $(I_{I}/I_{I}) = (I_{I}/I_{I})$ can be read	
	from which α can be estimated	86
Fig. 4	Schematic diagram of the experimental apparatus used in	
	this study. L is a laser light source, P is a pinhole,	
	M is a mirror, MC is a microcouette apparatus which	
	consists of two plates. The upper one is stationary	
	and the lower one rotates at an adjustable rotational	
	velocity Ω . The plates are separated by a distance <i>l</i>	
	and the distance from the center of the plates to where	
	the laser passes through the cell is r. PH is a photo-	
	diode, PM is a photomultiplier, DAS is a data acquisi-	
	tion system and PC is a personal computer	90
Fig. 5	Illustration of the procedure used to correct for the	
	scattering due to the glass/oil and glass/air inter-	
	faces.	
	(a) The case when pure silicone oil is present.	
	(b) The case when the emulsion is present in the cell \dots	91
Fig. 6	The flow pattern in the system of two plates where	
	the upper one is stationary and the lower one rotates	
	at an angular velocity Ω for the case where Re = $\rho_0 v_{\rho} l/\mu_0$	
	<< 1.0	93
Fig. 7	Experimentally measured I_t/I_t versus time for water/	
	silicone oil emulsion sheared at 10 s ⁻¹	96
Fig. 8	Experimentally measured I_t/I_c versus time for water/	
	silicone oil emulsion in the absence of shear ($G = 0$)	97

C

Page

Fig. 9	A plot of α versus the dimensionless number Gt for	1 4
	water/silicone oil emulsion sheared at 10.0 s^{-1} . The	
	value of the critical radius, a_c , above which $\alpha_c = 0$	
	is 2.0 μ m. \bullet , o, Δ and \blacktriangle correspond to $(\overline{a}, \sigma) = (0.34, \sigma)$	
	0.01), (0.57, 0.01), (0.11, 0.70) and (0.30, 0.35),	
	respectively. The curve shown by s is the result ob-	
	tained for a bimodal distribution	101
Fig. 10	A plot of standard deviation, σ , versus the mean	
	radius, \overline{a} , for log normal distributions whose max-	
	imum radius is 6.5 μ m and which give a range of	
	I_t/I_a between 0.2 and 0.4. Points a, b, c and d	
	correspond to $(\bar{a}, \sigma) = (0.34, 0.01), (0.57, 0.02).$	
	(0.11, 0.70) and (0.3, 0.35), respectively	102
Fig. 11	A plot of α versus the dimensionless number Gt for	105
	water/silicone oil emulsion sheared at 199 s ⁻¹ . The	
	value of the critical radius, a , above which $\alpha =$	
	0 is 2.0 μ m. ϕ , \clubsuit , ∇ and ∇ correspond to $(\overline{a}, \sigma) =$	
	(0.34, 0.01), (0.57, 0.01), (0.11, 0.71) and (0.3)	
	0.35), respectively. The curve shown by Corre-	
	sponds to the results obtained for the bimodal	
	distribution	104
Fig. 12	A plot of α versus the dimensionless number Gt for	104
	water/silicone oil emulsions of a log normal distri-	
	bution $(\bar{a}, \sigma) = (0.34, 0.01), (0.57, 0.01)$ and (0.11)	
	(0.70) and having a maximum size of 6.5 up channel.	
	199 s ⁻¹ for the cases where a is 1.5, 2.0 and 2.5	
	and ∇ are for the cases where $(\overline{a}, \overline{c}) = (0, 24, 0, 04)$	
	and $(0.57, 0.01)$, respectively, where $(a, b) = (0.34, 0.01)$	
	of α on a was found \mathbf{A} $\mathbf{\nabla}$ and $\mathbf{\nabla}$ are for (\mathbf{T})	
	(0.11, 0.70) for a = 1.5, 2.0 and 2.5 µm, respectively	
	tively, where dependence within $\pm 0.2\%$ of α on a	
	can be observed	101
Fig. 13	The effect of the value of the constant C on the	106
	coalescence efficiency coefficient. For values of C	

.

Page

-

.

between 0 and 6, α_c changes with ± 2%. The values of	
α were calculated for $(\overline{a},\sigma) = (0.30 \ \mu\text{m}, 0.35)$ and	
$G = 10 s^{-1}$	108

APPENDIX 3-C

CHAPTER 4

Fig.	1	The change in experimentally measured light transmit-	
		tance intensity, $(I_{1}/I_{2})_{even}$, versus time for water/	
		silicone oil emulsions sheared at $G = 18 \text{ s}^{-1}$. The	
		viscosity of the silicone oil is 97 mPas	137
Fig.	2	The change in the experimentally measured light trans-	
		mittance intensity, $(I_{t}/I_{o})_{exp}$, versus time for water/	
		silicone oil emulsion sheared at $G = 10 \text{ s}^{-1}$. The water	
		phase contains 1.34 M KCl. the viscosity of the sili-	
		cone oil is 97 mPas	138
Fig. 3	3	The change in the experimentally measured light trans-	
		mittance intensity, $(I_{\downarrow}/I_{\downarrow})_{even}$, versus time for water/	
		olive oil emulsion sheared at 10 s^{-1} . The oscillations	
		appearing in the figure are due to imperfect adjustment	
		of the plates	139
Fig. 4	4	The coalescence efficiency coefficient versus Gt for	
		water/silicone oil emulsion subjected to various shear	
		rates calculated for C = 1.0 and $a_c = 2.0 \ \mu m$. The	
		viscosity of the silicone oil is 97 mPas	145
Fig. 5	5	The coalescence efficiency coefficient versus G for	
		water/silicone oil emulsion at $t^* = 0$. Calculated	
		for C - 1.0 and $a_c = 2.0 \ \mu m$. The viscosity of the	
		silicone oil is 97 mPas	146

Page

			Page
Fig.	6	The dependence of α on the dimensionless number C	
		where the dimensionless number Ca is a parameter is	
		qualitatively shown	149
Fig.	7	The collision efficiency coefficient versus Gt for	
		water/silicone oil emulsion subjected to various	
		shear rates calculated for C = 1.0 and a = 2.0 μ m.	
		The water phase contains 13.4 mM KCl. The viscosity	
		of the silicone oil is 97 mPas.	
Fig.	8	The collision efficiency coefficient versus Gt for	
		water/silicone oil emulsion subjected to various	
		shear rates calculated for C = 1.0 and a_{c} = 2.0 μ m.	
		The water phase contains 7.5 mM AlCl ₃ . The vis-	
		cosity of the silicone oil is 97 mPas	152
Fig.	9	The coalescence efficiency coefficient versus Gt for	
		water/silicone oil emulsion subjected to various	
		shear rates calculated for C = 1.0 and a_{c} = 2.0 μ m.	
		The water phase contains 3.5 mM SDS. The viscosity	
		of the silicone oil is 97 mPas	153
Fig.	10	The coalescence efficiency coefficient versus G for	
		water/silicone oil emulsion at $t^* = 0$ calculated for	
		C = 1.0 and $a_c = 2.0 \ \mu m$. The water phase contains	
		13.4 mM KCl. The viscosity of the silicone oil is	
		97 mPas	154
Fig.	11	The coalescence efficiency coefficient versus G for	
		water/silicone oil emulsion at $t^* = 0$ calculated for	
		$C = 1.0$ and $a_c = 2.0 \ \mu m$. The water phase contains	
		7.5 mM AlCl ₃ . The viscosity of the silicone oil is	
		97 mPas	155
Fig.	12	The coalescence efficiency coefficient versus G for	
		water/silicone oil emulsion at $t^* = 0$ calculated	
		for C = 1.0 and $a_c = 2.0 \ \mu m$. The water phase con-	
		tains 3.5 mM SDS. The viscosity of the silicone oil	
		is 97 mPas	156

xi

.

Fig. 1	13	The effect of the concentration of KCl on the coa-	
		lescence efficiency coefficient as a function of Gt	
		for water/silicone oil emulsion sheared at G = 10 s^{-1} .	
		The calculations were done for $C = 1.0$ and $a_c = 2.0$	
		μ m. The viscosity of the silicone oil is 97 mPas	158
Fig. 1	14	The experimentally obtained coalescence efficiency	
		coefficient at $t^* = 0$ versus the concentration of	
		KCl for water/silicone oil emulsions sheared at G =	
		10 s ⁻¹ . The calculations were done for $C = 1.0$ and	
		a = 2.0 μ m. For comparison, interfacial tensions	
		are shown as well	160
Fig. 1	15	The coalescence efficient coefficient versus Gt for	
		water/silicone oil and water/olive oil emulsions	
		sheared at 10 s ⁻¹ . The calculations were done for	
		$C = 1.0 \text{ and } a_{2} = 2.0 \ \mu m.$	
Fig. 1	16	The coalescence efficiency coefficient versus Gt for	
		water/silicone oil and water contains 50 g gold part-	
		icles/L - silicone oil emulsions sheared at 10 s^{-1} .	
		The calculations were done for $C = 1.0$ and $a_{1} = 2.0$	
		c μm	165

C

Page

CHAPTER 5

Fig. 1	Initial log normal droplet radius distribution divided	
	into classes. The mean radius and the standard devi-	
	ation are 0.3 μ m and 0.35, respectively	177
Fig. 2	The collision frequency, F_{ij} , between a droplet of	
	radius a and droplet in class j calculated by Eq.	
	[1]. The droplet radius distribution is log normal	
	\overline{a} = 0.3 µm and σ = 0.35. The value of a_{1} = 0.345 µm	179
Fig. 3	The cumulative droplet radius distribution for the	
	log normal distribution given in Fig. 1. A point P	
	on the figure determines a random choice of class i	182
Fig. 4	The initial droplet radius distribution given in	
	Fig. 2, shown by open circles, is compared to a	

		randomly obtained distribution, shown by the solid	
		line. 1000 random classes were used to regenerate	
		the initial distribution	183
Fig.	5	Changes in the droplet radius distribution as col-	
		lisions proceed. The values of \overline{a} , σ , a and C are	
		0.3 μ m, 0.35, 2.0 μ m and 5, respectively	186
Fig.	6	Changes in the initial droplet radius distribution as	
		collisions proceed. The values of \overline{a} , σ , a and C are	
		0.3 μm, 0.35, 2.0 μm and 0, respectively	187
Fig.	7	The change in $(N_{p} - N_{t})/N_{p}$ versus C for various values	
		of η . the droplet radius distribution is as given in	
		Fig. 1	188
Fig.	8	Changes in the initial droplet radius distribution as	
		collisions proceed. The values of \overline{a} , σ , a and C are	
		0.3 μm, 0.6, 2.0 μm, and 5, respectively.	
Fig.	9	Comparison between N_t/N_c versus F_t/F_c obtained by	
		direct solution of Smoluchowski's equation and Monte	
		Carlo method	191
Fig.	10	The cumulative droplet radius distribution given in	
		Fig. 1 versus ξ for all values of η . The results	
		are applicable for any value of C. The difference	
		is within the thickness of the line. The figure	
		shows that the distribution is self-preserved	195
Fig.	11	The log normal cumulative droplet radius distribu-	
		tion of \overline{a} = 0.3 μ m and σ = 0.6 versus ξ for all	
		values of η and C. The difference is within the	
		thickness of the line. The self-preserving form	
		can be seen from the above curves	196

LIST OF TABLES

C

CHAPTER 2

Table 1	List of refractive indices of water, silicone oil	
	and latex at 25°C	38
Table 2	Comparison between the experimental results for	
	latex dispersion and the ones provided by the	
	supplier	44
Table 3	List of experimentally measured and theoretically	
	calculated values of (T_n/T_n) at the wavelengths	
	indicated in column 1 for the monodisperse latex-	
	water suspension	45
Table 4	Comparison between the experimental results for	
	latex dispersions and the ones provided by the	
	supplier	45
Table 5	Comparison between the results of Glenhill electron	
	microscopy, EM, and this method	47

CHAPTER 4

Table 1	List of the refractive index ratio of the droplets to	
	that of the continuous medium, m, and the interfacial	
	tension between the two phases of the emulsion mea-	
	sured at 23°C	136
Table 2	A list of the value of $(I_t/I_o)_{exp}$ for the systems	
	shown in column 1, the applied shear rate,	
	$(I_t/I_o)_{exp} - E_1, (I_t/I_o)_{exp} + E_2, a, b, c and d \dots$	141

Page

.

CHAPTER 1

.

INTRODUCTION

GENERAL REMARKS

Emulsions are defined as multiphase systems, where at least one liquid phase is dispersed in another liquid phase in the form of droplets. Thermodynamically, emulsions are unstable systems. Their stability is a very crucial point for many industrial processes. For example, all cosmetic, food and pharmaceutical emulsions are required to be very stable for a long period of time. On the other hand, in the production of crude oil from tar sands, the oil is produced as a water in oil emulsion (1,2). Hence it is necessary to separate the water phase from the oil phase before it is processed.

Emulsions are usually stabilized by adding surfactants, fine solids and various sorts of additives (3,4). In the presence of these stabilizers the repulsive forces, which keep the droplets apart and prevent coalescence, dominate the attraction forces. The coalescence process requires that the droplets collide with each other and coalesce. This raises the question: what is meant by a collision? Consider a droplet of radius a_i approaching another droplet of radius a, due to the presence of a shear flow of gradi-The appropriate coordinate system in this case is a Cartesian coorent G. dinate system which is drawn such that its center coincides with the center of droplet a (see Fig. 1a). The collision cross section for these droplets is a sphere whose radius is $a_i + a_j$. According to Smoluchowski, if the center of the droplet a_i passes through the capture cross section then a collision will occur. If a is captured by a_i the collision is termed successful (Fig. 1b), otherwise the collision is not successful (Fig. 1c). Thus one can define a collision or coalescence efficiency, α , as

Fig. 1 The collision process between two droplets approaching each other in simple shear flow is shown.

(a) If the center of sphere a_j does not pass through the collision sphere shown by a sphere of radius $a_i + a_j$ then no collision occurs. If sphere a_j passes through the collision sphere then a collision occurs.

(b) If sphere a_j is captured by the central sphere then the collision is termed successful and leads to coalescence.

(c) If sphere a_j collides with the central sphere and is still not captured, then the collision is termed unsuccessful and no coalescence occurs.



$\alpha = \frac{\text{number of collisions leading to coalescence}}{\text{total number of collisions}}$ [1]

The collision efficiency is a function of many variables such as: The viscosity of the continuous medium, its dielectric constant, the surface potential of the droplets, the Hamaker constant of the system, the radii of the colliding droplets, the shear rate and the interfacial tension.

The collision beteen two emulsion droplets can be caused by the action of a shear flow. In this case the collision efficiency is termed orthokinetic collision efficiency and will be denoted throughout the thesis by α_{o} . If the collision is caused by Brownian motion of the droplets then the collision efficiency is called *perikinetic collision efficiency* and will be denoted by α_{p} . In the following section the orthokinetic collision efficiency will be discussed in more detail.

The Orthokinetic Collision Efficiency

Consider a droplet of radius a_i at the center of a Cartesian coordinate system. This sphere is called the central or reference sphere. A sphere of radius $a_i + a_j$ around the reference sphere is called the collision sphere (see Fig. 2). A quadrant of the projection of the collision sphere is shown in Fig. 2. The flux of droplets, j, through any section of this quadrant is

$$j = u_{y}n$$
, [2]

where n is the number of droplets per unit volume and u_x is the x-component of the velocity. The total flux, J, is

Fig. 2 A central sphere of radius a_i and a collision sphere of radius a_i + a_j are shown. The center of both spheres is the center of a Cartesian coordinate system. A sphere of radius a_j approaching a_i from ∞ in simple shear flow is also shown. If a_i passes through the quadrant shown in the figure, then it will collide with the central shere.



C

u_x=Gz

,

$$J = 4 \int j dA .$$
A
[3]

Note that the integral is multiplied by 4 because there are 4 quadrants. Substituting Eq. [2] in Eq. [3] and noting that $u_x = Gz$, Eq. [3] becomes

$$J = 4Gn \int zdA .$$

$$A$$
[4]

The rate of change of n with time, t, is nJ/2, or

$$\frac{dn}{dt} = -2Gn^2 \int zdA .$$

$$[5]$$

The minus sign appearing in Eq. [5] is to indicate that the number of particles decreases with time due to coalescence.

Taking into account the interaction forces between colloidal particles, Smoluchowski's coagulation equation, which describes the rate of change of n particles of radius a with time, was corrected by introducing the collision efficiency as (5)

$$\frac{\mathrm{dn}}{\mathrm{dt}} = -\frac{16}{3} \operatorname{Gn}^2 a^3 \alpha_{\alpha} .$$
^[6]

Comparing Eq. [5] with Eq. [6] shows that α_{o} can be expressed as

$$\alpha_{o} = \frac{3}{8a^{3}} \int z dA .$$
 [7]

For a particular system the magnitude of α_{o} can be derived from the exact form of the boundary (z) of the capture cross section.

Several authors (5-7) have calculated the boundaries of the capture cross section by solving the trajectory equations of particles in shear flow written as (8)

$$\frac{dr}{dt} = \bar{a}GA(r,q)\sin^2\theta\sin^2\phi + \frac{F_{coll}C(r,q)}{3\eta\mu\bar{a}} , \qquad [8a]$$

$$\frac{d\theta}{dt} = \frac{1}{4} GB(r,q)\sin 2\theta \sin 2\phi , \qquad [8b]$$

$$\frac{d\phi}{dt} = \frac{1}{2} G \left(1 + B(r,q)\cos 2\phi \right) , \qquad [8c]$$

where q is the radius ratio of the colliding droplets and (r, θ, ϕ) are the polar coordinates. For hard spheres, A, B and C are known functions of r and q. F_{coll} is the net colloidal force acting on the droplets, $t^* = Gt$ is the dimensionless time and $\bar{a} = (a_1 + a_2)/2$. For the case where the electrical repulsive forces are negligible and for equal size particles, van de Ven and Mason (5) showed that α can be expressed by

$$\alpha_{o} = f(\lambda) C_{A}^{0.18} , \qquad [9]$$

where $\boldsymbol{C}_{_{\!\boldsymbol{A}}}$ and $\boldsymbol{\lambda}$ are dimensionless variables given by

$$C_{A} = \frac{A}{36\eta\mu G\bar{a}^{3}} , \qquad [10]$$

$$\lambda = \frac{\lambda}{2\pi \bar{a}} , \qquad [11]$$

 λ being the London wavelength. C represents the ratio of the attraction forces to the hydrodynamic forces.

In the presence of repulsive forces, the picture is different. As the shear rate increases α_0 decreases until a critical shear rate is reached where it drops rapidly. A further increase in G causes α_0 to increase until another critical G is reached, after which it decreases upon further increase in G.

In the case of particles with unequal radii, Adler (9) and Shinoda et al. (10) showed qualitatively the same results obtained earlier by van de Ven and Mason (5). Fig. 3 shows a qualitative dependence of α_{o} on the parameter C_{A} . The parameter C_{R} appearing in Fig. 3 is a measure of the repulsive forces to that of the hydrodynamic forces and is given by

$$C_{R} = \frac{2\varepsilon \varepsilon_{v} \psi^{2}}{3\mu G \bar{a}^{2}} , \qquad [12]$$

where ε and ε_{o} are the permittivity of the suspending fluid and free space, respectively, ψ_{o} is the surface potential of the sphere and μ is the viscosity of the continuous medium. It has recently been shown that the trajectory equations [8a-c] are incomplete, since electroviscous forces arising from a coupling between electrostatics and hydrodynamics are omitted (11).

It should be noted that, in general, α_{o} for two particles of equal radius is higher than that of particles of unequal radius, i.e. usually homocoagulation is favored over heterocoagulation. However, under certain

Fig. 3 The dependence of α_{o} on the dimensionless number C_{A} where the dimensionless number C_{R} is a parameter is qualitatively shown. In the absence of repulsion forces ($C_{R} = 0$), α_{o} increases as C_{A} increases. In the presence of repulsive forces ($C_{R} > 0$) α_{o} versus $\log(C_{A}^{-1})$ goes through a minimum and maximum consecutively.



C

 $Log(C_A^{-1})$

conditions the opposite can be true (9). The reason for this is that the trajectories of two particles in shear flow, resulting from solving Eqs. [8] can be divided into open trajectories, closed trajectories and limiting trajectories. In the absence of colloidal interaction forces and Brownian movement, a particle can never approach closer than a minimum distance d_{min} . This minimum distance can be defined as the minimum distance of approach between a particle which is located on the limiting trajectory and the central particle, as can be seen from Fig. 4. d_{min} is a strong function of the radius ratio (12). As the radius ratio increases (the maximum value of the radius ratio is 1 when the two colliding droplets have equal radii) d_{min} is small and the effect of colloidal forces is more pronounced. Therefore the orthokinetic collision efficiency is high. As the radius ratio approaches zero, α_o approaches zero as well, since in that limit d_{min} is much larger than the distance over which colloidal forces are acting.

One of the objectives of this thesis is to investigate the collision efficiency and its dependence on the radius ratio of the emulsion droplets. An approximate relation for such dependence will be proposed based on the observations of (5), (9) and (12).

Orthokinetic Collision Efficiency in Various Shear Flows

In this section we discuss the effect of various forms of shear on the orthokinetic collision efficiency.

1. Flow in a tube:

Consider a tube of radius R. The velocity distribution as a function of the radial distance, r, is

$$v_{\rm r} = v_{\rm max} [1 - (r/R)^2],$$
 [13]

Fig. 4 The trajectories of a sphere a_2 approaching another sphere a_1 in simple shear flow is shown. These trajectories can be divided into open trajectories and closed trajectories. The two types of trajectories are separated by a limiting trajectory. The minimum distance, d_{min} , a_2 can approach a_1 is also shown.



and the shear rate $G = |dv_r/dr|$ can be obtained by taking the derivative of Eq. [13] with respect to r. This yields

$$G = \frac{2v_{max}r}{R^2} .$$
 [14]

The average shear rate in the tube, <G>, is

,

$$\langle G \rangle = \frac{1}{A} \int_{A} G dA = \frac{4\pi v_{max}}{\pi R^4} \int_{0}^{R} r^2 dr = \frac{4v_{max}}{3R} , \qquad [15]$$

since

$$v_{max} = 2 \langle v \rangle = \frac{2Q}{\pi R^2}$$

then <G> takes the following form

$$\langle G \rangle = \frac{8Q}{3\pi R^3} .$$
 [16]

In the above equations v_{max} is the maximum velocity at the center of the tube, $\langle v \rangle$ is the average velocity, Q is the volumetric flow rate and R is the radius of the tube. Substituting Eq. [16] into Eq. [6] we obtain

$$\frac{dn}{dt} = -\frac{1280}{9\pi R^3} a^3 n^2 \alpha_0 .$$
 [17]
2. Flow between two coaxial cylinders

Consider two coaxial cylinders where the outer cylinder is stationary and the inner one rotates at an angular velocity Ω . Let the radius of the outer cylinder be R_o and the inner one R_i. Solving the Navier-Stokes equation leads to the following dependence of the velocity in the θ -direction, v_{θ}, on r

$$v_{\theta} = \frac{\Omega R_{1}^{2} R_{0}}{R_{1}^{2} - R_{0}^{2}} [(r/R_{0}) - (R_{0}/r)] . \qquad [18]$$

Again the shear rate G is $|dv_{\theta}/dr|$ and from Eq. [18] one obtains:

$$G = \frac{\Omega R_{i}^{2}}{R_{o}^{2} - R_{i}^{2}} \left[1 + (R_{o}/r)^{2}\right] .$$
[19]

The average shear is

$$\langle G \rangle = \frac{\Omega R_{i}^{2}}{R_{o}^{2} - R_{i}^{2}} \left[1 + \frac{2R_{o}^{2}}{R_{o}^{2} - R_{i}^{2}} \ln \left(R_{o} / R_{i} \right) \right].$$
 [20]

Substituting Eq. [20] in Eq. [6], the rate of change of n with time becomes

$$\frac{dn}{dt} = -\frac{16\Omega R_{i}^{2} R_{a}^{2}}{3(R_{o}^{2} - R_{i}^{2})} \left[1 + \frac{2R_{o}^{2}}{R_{o}^{2} - R_{i}^{2}} \ln(R_{o}/R_{i}) \right] \alpha_{o} .$$
[21]

In the case where the inner cylinder is stationary and the outer one

is rotating at an angular velocity Ω , the rate of change of n is given by

$$\frac{dn}{dt} = -\frac{16\Omega R_o^2 n^2 a^3}{3(R_o^2 - R_i^2)} \left[1 + \frac{2R_i^2}{R_o^2 - R_i^2} \ln(R_o/R_i) \right] \alpha_o .$$
[22]

We should note that Eqs. [17], [21] and [22] were derived assuming that α_{o} is constant, i.e. independent of the shear rate. In general this assumption is not true since α_{o} is a function of G. In this case $\langle G \rangle \alpha_{o}$ should be replaced by $\langle G \alpha_{o} \rangle$, or $\int rG(r)\alpha_{o}(r)dr/\int rdr$. However over a certain range of shear rates where α_{o} is independent or weakly dependent on G the above analysis can be used. In Chapter 4 of this thesis the effect of G on α_{o} will be discussed from an experimental and theoretical point of view.

Smoluchowski's Coagulation Equation for Polydisperse Systems

Eq. [6] was derived for two equal particles. When the system is polydisperse the equation can be rewritten, taking the following considerations into account. Let us divide the initial distribution into classes i with radius and number of particles a_i and n_i , respectively. Upon coagulation, the concentration of particles with small radii decreases. On the other hand, the number of particles that belong to a class with larger radius increases. If coagulation is solely due to shear flow the rate of change of the number of droplets, n_i , is given by

$$\frac{dn_{i}}{dt} = -\frac{4}{3} G \left[\frac{1}{2} \sum_{j+k=i}^{\sum} n_{k} n_{j} (a_{k} + a_{j})^{3} \alpha_{jk} - n_{i} \sum_{j=1}^{j=1} n_{j} (a_{i} + a_{j})^{3} \alpha_{ij} \right],$$
[23]

where I is the total number of classes. The first term on the right hand

side of Eq. [23] is the production term and the second term corresponds to the depletion term of n_i ; α_{ij} is the is the collision efficiency for a collision between a particle of radius a_i and one of radius a_j .

Ultrasonic Emulsification

Ultrasonic emulsification is the employment of ultrasonic waves at the interface between two liquids. Dispersion of one liquid into the other one is a result of one or a combination of any of the following mechanisms (13,14): (i) cavitation, (ii) interfacial instability, (iii) microstreaming, and (iv) transverse oscillation of the walls of the vessel in which emulsification is taking place. There is a great disagreement in the literature about which one of the above mechanisms is the cause for emulsification, but it is widely accepted that both cavitation and interfacial instabilities are the main causes of emulsification.

Cavitation is the subsequent growth and collapse of bubbles in Therefore the presence of dissolved gases is essential for liquids. cavitation to occur (15). Cavitation does not take place until the liquid pressure has become sufficiently negative to overcome the surface tension forces. The cavitation intensity is a function of the frequency, bubble radius, pressure of the liquid and the pressure inside the bubble (16,17). It increaes as the bubble radius, the pressure of the liquid, and the pressure inside the bubble increase. Conversely, it decreases as the frequency increases. Everything being equal, there is a limiting bubble size below which cavitation cannot occur because surface tension forces prevent it Moreover, there are minimum and maximum threshold values from growing. below and above which cavitation does not occur (18). At a certain pressure, as the frequency increases, the upper threshold for cavitation ap-

proaches the lower one until it coincides with it. At a higher frequency, cavitation no longer occurs. The physicochemical properties of the emulsion components have a considerable effect on the emulsification process. These properties are: viscosity ratio, density difference, interfacial tension, presence of dissolved gases and surface active agents. They affect the values of the threshold intensity and the emulsification rate.

The second important mechanism by which dispersion of liquids takes place is the occurrence of instabilities set up at the interface between two liquids. Rayleigh-Taylor instabilities and Kelvin-Helmoltz instabilities are examples of such instabilities. A Rayleigh-Taylor instability occurs when acceleration of the lighter liquid to the heavier liquid takes place. Due to this the interface becomes unstable and disruption of the interface happens. A Kelvin-Helmoltz instability is the result of a tangential velocity difference at the interface.

Whether cavitation or surface instabilities are the reasons for emulsification, the dispersion of one liquid in the other proceeds as follows (19). When the ultrasonic waves are applied at the interface between two liquids, masses of one liquid penetrate in the other. These masses grow in size and eventually break from the main interface forming droplets. These large droplets, in turn, serve as a new interface which continues to break. The breaking off of the large droplets is usually accompanied by formation of much smaller droplets called satellite droplets. In light of this, formation of a polydisperse emulsion is expected. This process is schematically depicted in Fig. 5.

Fogler (20) and Neduzhii (21) claimed that if enough ultrasonification time is applied, a limiting droplet size will eventually be reached. Many attempts have been made to correlate the droplet radius to the working

parameters of the ultrasonic waves, such as the frequency of the sound waves, its amplitude and intensity, etc. No attention will be given here to the results of these attempts, but one can refer to (22-24) for more details about this point.

For the purpose of the research reported in this thesis, ultrasonic emulsification was used to prepare the emulsions. The frequency, intensity and the power input were all fixed and they are properties of the ultrasonic bath that was used. This assures that all the emulsions prepared for the purposes of the experiments discussed throughout the thesis are prepared in the same manner. This does not imply that the emulsions prepared were the same. In fact it was found from the transmitted light intensity measurements that every time an emulsion is prepared, a different droplet radius distribution is produced. Determination of the initial droplet radius distribution by conventional methods was found to be impossible. The reasons for this are discussed in Chapter 2. Thus a new technique had to be developed to determine the droplet size distribution. This technique is based on measuring transmitted light intensity through the emulsion as a function of wavelength of the light beam. The method was tested in various ways and it was concluded that it is successful in obtaining the size distribution. Although we succeeded in determining the radius distribution of the emulsion droplets, it was a very difficult task to do before every shear-induced coalescence experiment. This is due to the fact that the two experimental set-ups were placed in two different buildings and it was feared that the initial droplet radius distribution would change due to the elapsed time necessary to perform the size distribution experiment and to the changes that might take place while transferring the emulsion to the testing cell.

Fig. 5 The process of forming a droplet by applying ultrasonic waves at the interface between two immisible liquids is depicted.(a) The two phases before the application of the ultrasonic waves.

(b) Mass of liquid I penetrates liquid II upon the application of ultrasonic waves.

(c) Formation of a large droplet followed by small sattelite droplets. t=0 liquid I liquid I (b) t=t1 mass of liquid I penetrating liquid I ultrasonic waves

(a)

(c)

t>t1 main droplet satellite droplets The solution to this problem is discussed in detail in Chapter 3. It was found, within a certain droplet size range, that the orthokinetic collision efficiency is a weak function of the initial droplet radius distribution. These results were deemed sufficient and thus repeated determination of the initial droplet radius distribution was unnecessary.

In Chapter 4 the effect of additives such as surface active agents, solid particles, electrolytes, the effect of the applied shear rate and the interfacial tension were discussed. It was found that emulsions can be stabilized, or the coalescence efficiency can be decreased by (i) adding solid particles, (ii) decreasing the interfacial tension by adding surfactants, electrolytes, etc., and (iii) working under a certain range of shear rate.

In Chapter 5 a Monte Carlo simulation method was used to simulate coalescence of emulsion droplets in shear flow. The self-preserving form hypothesis was tested.

The chapters of the thesis are written such that they are completely independent of each other. Every chapter has its own abstract, introduction, theory, results, conclusions, references, nomenclature and appendices. Special care was made such that the nomenclature utilized are the same in all chapters. Thus every chapter of this thesis is a complete work and serves as a paper ready for submission to a scientific journal.

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NOMENCLATURE

C

а	- radius of the colloidal particles, m.
Α	- area, m ² . Constant used in Eqs. [8], dimensionless Hamaker
	constant, J
В	- constant used in Eqs. [8], dimensionless.
С	- constant used in Eqs. [8], dimensionless.
C_	- ratio of attraction forces to hydrodynamic forces given in Eq.
	[10], dimensionless.
C R	- ratio of repulsive forces to hydrodynamic forces given in Eq.
	[12], dimensionless.
F coll	- colloidal force, N.
G	- shear rate, s ⁻¹ .
j	- flux of particles, $s^{-1}m^{-2}$.
J	- total flux of particles, s ⁻¹ .
n	- number of particles per unit volume, m^{-3} .
q	- particle radius ratio, dimensionless.
Q	- volumetric flow rate, m ³ /s.
r	- r-component of the polar coordinate system, m.
R	- radius of a tube, R _i : inner radius, R _i : outer radius, m.
t	- time, s.
u x	- x-component of the velocity, m/s.
v _r	- r-component of the velocity, v : maximum velocity at the
	- center of the tube, <v>: average veelocity, m/s.</v>
x	- x-component of a Cartesian coordinate system, m.
У	- y-component of a Cartesian coordinate system, m.
z	- z-components of a Cartesian coordinate system, m.

C

Greek

α	- collision efficiency, dimensionless.
3	- permittivity of the suspending fluid, dimensionless.
ε _θ	- permittivity of free space, Farad/m.
¢	- ϕ -component of the polar coordinate system.
λ	- London wavelength, m.
λ	- dimensionless London wavelength given in Eq. [11].
μ	- viscosity of the medium, Pas.
ψ	- surface potential of the sphere, V.
θ	- θ -component of the polar coordinate system.
Ω	- angular velocity, rad/s.

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CHAPTER 2

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TURBIDIMETRIC DETERMINATION OF PARTICLE SIZE DISTRIBUTIONS

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ABSTRACT

A method was developed to determine the particle size distribution of an emulsion or a dispersion which applies equally to monodisperse and highly polydisperse colloidal systems. The method is based on measuring the intensity of the light transmitted through the colloidal system as a function of wavelength. A suitable form of the particle size distribution that can represent the colloidal system must be assumed. The method was tested on both monodisperse and bimodal distributions of latex particles and on polydisperse water in oil emulsions. These tests showed that the method is simple, highly accurate and reliable. By making various guesses about the form of the actual distribution, i.e. log normal, Gaussian, gamma, bimodal, etc., one can select the distribution that best fits the actual distribution by minimizing the difference between experimentally measured and either theoretically calculated turbidity ratios or light This method is extremely fast, accurate and transmitted intensities. requires less experimental effort than other methods. It eliminates many experimental problems which could alter the particle size distribution of the colloidal system to be tested.

INTRODUCTION

Many techniques are available in the literature to determine the particle size distribution of colloidal systems. Experimental limitations, cost, and the nature of the assumptions involved, make the application of many of these methods difficult. A nice review of the different problems encountered in the classical methods for the determination of the particle size distribution can be found in refs. (1,2). Brill et al. (3) and Letcher and Schmidt (4) used a small angle X-ray scattering method applicable to particles below 0.1 μ m. Thomas (5) applied dynamic light scattering (photon correlation spectroscopy or PCS) to determine log normal particle size distributions. He found that the method is good only for small particles (< 0.5 μ m) and for narrow distributions. Beyer (1) and Bowen et al. (6) described an optical pulse particle size analyzer based on measuring the scattered light intensity as the particles pass through a light This method is very expensive to use and requires that the system beam. to be tested is highly diluted which is not suitable for systems whose stability could be altered by dilution.

One example to which all of the above techniques of the particle size determination cannot be applied is a water in oil emulsion. Microscopic analysis of the size of the emulsion droplets may be inaccurate either when the droplets are below 1 μ m in diameter or when the refractive index difference between the two phases of the emulsions is small, which is the case, e.g., for water/silicone oil emulsions. In any of these cases the emulsions droplets cannot be clearly seen under the microscope. When the continuous medium of the emulsion is very viscous, the Brownian motion of

the suspended droplets is too small to allow detection by PCS and, therefore, obtaining the mean radius of the distribution by this method is not feasible. Furthermore, PCS can find the standard deviation reliably only when the colloidal system has a narrow size distribution. Water/oil and oil/water emulsions formed by ultrasonics are usually highly polydisperse due to the random nature of the break-up of the interface between the oil and the water phases (7).

All of the above difficulties, as well as many others in determining particle size distributions, lead us to think of other ways to obtain the droplet size distribution.

Hiemenz and Vold (8) developed a method for obtaining the relative sizes of flocs of carbon black dispersions based on measuring specific optical densities and the wavelength exponent. Their method is useful for cases where the Mie theory, which describes the scattering from a single spherical particle, is inadequate. Furthermore, their method requires that the size of the individual particles is known from some other tech-Gledhill (9) and Melik and Fogler (10) developed similar methods nique. for the determination of the particle size distribution by turbidimetry. The methods are based on measuring the specific turbidity and the logarithmic slope which Melik and Fogler called the wavelength exponent. The two methods are similar except for the analysis to estimate the particle size distribution. A brief discussion of the method will be given in the section dealing with comparison of our method with other turbidimetric methods.

In this chapter a method is developed similar to that of (9) and (10), based on comparing either experimentally measured and theoretically calcu-

lated light transmitted intensities or turbidity ratios at various wavelengths passing through the colloidal system. It differs from other turbidimetric methods in that it eliminates the need for a logarithmic slope or a wavelength exponent which requires very tedious mathematical calculations and a long computation time. The need for the logarithmic slope was replaced by an extra turbidity measurement at a different wavelength in the case where turbidity ratios were used. Thus, at least three turbidity measurements at three different wavelengths are required.

The technique was applied to a highly polydisperse water/oil emulsion and tested experimentally on suspensions of monodisperse and bimodal distribution of latex particles and on experimental data obtained from (9). It is very simple and quick to apply. It involves only one assumption regarding the nature of the distribution governing the colloidal system, i.e. log normal, Gaussian, etc. In some cases, more than one type of distribution can reasonably describe the colloidal system. In this case the method allows one to choose between different types of distributions by choosing the one which gives the minimum error.

THEORY

Let I_o be the intensity of the incident light which passes through a colloidal system. Some of this light will be either scattered or absorbed by the particles and the rest will be transmitted. The law of conservation of energy requires that the sum of the intensities of the transmitted light, I_t , the scattered ight, I_s , and the absorbed light, I_{abs} , must be equal to that of the incident light

$$\begin{bmatrix} = I + I + I \\ s & abs \end{bmatrix}$$
 [1]

The ratio I_t/I_o is given by (11)

$$I_t / I_o = \exp(-\pi l N \Sigma n_i^* Q_{ext,i} a_i^2) .$$
 [2]

If the colloidal system does not absorb light, then

$$Q_{ext,i} = Q_{s,i}$$
 [3]

Here *l* is the path length a light beam travels through the colloidal system, $n_{i}^{*} = n_{i}^{/N} = f(\bar{a},\sigma)$ is the fraction of the ith class particles whose radius is a_{i} and scattering efficiency $Q_{s,i}$. Q_{ext} is the light extinction coefficient, N is the total number of particles per unit volume, σ is the standard deviation and \bar{a} is the mean particle radius, i.e. the value below which 50% of the population falls.

The scattering efficiency, $Q_{s,i}$, is a function of particle radius, the ratio, m, of the refractive index of the particles to that of the continuous medium and the wavelength of light, λ . Q_s can be calculated from Mie scattering theory (12-14)

$$Q_{g} = (2/X^{2}) \sum_{n=1}^{\infty} (2n+1) \{ |a_{n}|^{2} + |b_{n}|^{2} \}, \qquad [4]$$

where

 $X = 2\pi a / \lambda_{med}$

$$a_{n} = \frac{A_{n}(y)\psi_{n}(X) - m\psi_{n}'(X)}{A_{n}(y)\xi_{n}(X) - m\xi_{n}'(y)},$$
[6]

[5]

101

$$b_{n} = \frac{mA_{n}(y)\psi_{n}(X) - \psi_{n}'(X)}{mA_{n}(y)\xi_{n}(X) - \xi_{n}'(X)},$$
[7]

$$y = mX ,$$
 [8]

$$A_{p}(y) = \psi_{p}'(y)/\psi_{p}(y)$$
, [9]

 ψ_n and ξ_n being Ricatti-Bessel's functions and Hankel's functions, respectively. The prime denotes the first derivative with respect to the argument. λ_{med} is the wavelength in the medium which is equal to λ/n_{med} where n_{med} is the refractive index of the continuous medium. Plots of Q_g versus X for different values of m are shown in Fig. 1. The functions ψ_n and ξ_n expressed in terms of spherical Bessel functions and the subroutine MISCAT that was written to calculate Q_g are shown in detail in Appendix 2-A and Appendix 2-B, respectively. The validity of the subroutine MISCAT was checked by inputting values for which results were reported previously (15).

In order to estimate the particle radius distribution of a colloidal system, one of the following procedures can be followed:

Procedure I

This procedure is based on comparing results of experimentally measured and theoretically calculated turbidity ratios as a function of the

Fig. 1 Calculated values of the scattering efficiency versus the dimensionless variable X for various values of the refractive index ratio m. 0



. . . wavelength. The advantage of this procedure is that it eliminates the need for the total number of colloidal particles, which is very difficult to obtain. Therefore it can be used for systems of unknown volume fraction or for systems where the total number of particles change with time. To eliminate the total number of particles in Eq. [2] from the calculations we adopted the following procedures. Taking the natural logarithm of Eq. [2] yields,

$$T_{n} = \ln (I_{t}/I_{o}) = -\pi IN \sum n^{*} Q_{s,i} (\lambda_{n}) a_{i}^{2}, \qquad [10]$$

where $(I_t/I_0)_n$ is the ratio of the transmitted light to that of the incident light measured at wavelength λ_n . For measurements that are done at λ_n and λ_m we can write

$$\frac{T_{m}}{T_{n}} = \frac{\sum n_{i}^{*}Q_{s,i}(\lambda_{n})a_{i}^{2}}{\sum n_{i}^{*}Q_{s,i}(\lambda_{n})a_{i}^{2}}.$$
[11]

This ratio no longer depends on the total number of particles N.

The disadvantage of this procedure, since it is based on the turbidity ratio, is that one can find an infinite number of distributions which give the same turbidity ratio as the experimentally measured one, but which does not necessarily yield the correct individual turbidities. For example, if we assume that the turbidities measured at λ_1 and λ_2 are 5 and 10, respectively, then the turbidity ratio would be 0.5. One can find an infinite number of values such as 4, and 8, 3 and 6, etc., which all have a turbidity ratio turbidities.

Thus one might obtain a set of distributions for which the difference between experimental and theoretical turbidity ratios (see Results and Discussion section), yet none of these distributions is close to the real one. For some unfortunate cases (e.g. the water/oil emulsion tested here) the distribution closest to the actual one might give a larger error compared to some other sets which can lead to incorrect conclusions. This possibility was not considered in previous work (8-10). Therefore we recommend procedure II to avoid this ambiguity.

Procedure II

This procedure is based on comparing experimentally measured and theoretically calculated light transmittance intensities. This procedure can be safely used if the volume fraction of the colloidal system is precisely known and for cases where the colloidal system is stable and no change in its number of particles occurs.

Particle Size Distributions

The first procedure was applied to a dispersion of monodisperse latex particles for which the volume fraction was not precisely known. The second procedure was applied to a bimodal distribution of latex particles and polydisperse water/oil emulsion.

Asuming a suitable form of the particle size distribution and dividing it into classes, the fraction of particles in each class can be calculated. The calculation of n_i^* for a log normal distribution will be illustrated below. For a log normal distribution the probability distribution function is given by

$$P(a) = \frac{1}{\sigma \bar{a} \sqrt{2\pi}} \exp\{- [\ln(a/\bar{a})]^2 / 2\sigma^2\}.$$
 [12]

The fraction of particles having a radius between a_i and a_{i+1} is

$$n_{i}^{*} = \int_{a_{i}}^{a_{i+1}} P(a)da = \frac{1}{2} \left[erf(Z_{i+1}) - erf(Z_{i}) \right], \qquad [13]$$

where

$$Z_{i} = \ln(a/\bar{a})/(\sigma\sqrt{2}) .$$
 [14]

Note that

$$\sum n_{i}^{*} = 1.0$$
 [15]

We should note that any other form of the distribution can be chosen as well, if that describes the particle distribution better. In such a case Eqs. [12]-[14] should be modified to suit the new distribution. Appendix 2-C shows the results for a Gaussian and a gamma distribution.

If the particles not only scatter light, but also absorb it, then the refractive index is a complex number, written as

$$n^* = n - ik$$
, [16]

where n and k are the real and the imaginary part of the refractive index, respectively, and $i = \sqrt{-1}$. Hence the extension coefficient becomes

$$Q_{\text{ext}} = Q_{\text{s}} + Q_{\text{abs}}$$
[17]

where Q_{abs} is the light absorption efficiency. In this case Eqs. [10] and [11] can be used by substituting the appropriate expessions for Q_{s} and Q_{abs} (16).

EXPERIMENTAL PART

The experimental apparatus is a Hewlet Packard 8451A DIOD ARRAY spec-A white light beam passing through the sample falls on a trophotometer. grating which disperses the light onto a photodiode array. Each diode measures the transmitted light intensity at a certain wavelength. The beam first passes through the reference material, placed in a square cuvette (1 cm x 0.4 cm x 5 cm), and the intensity at different values of λ varying from 190 nm to 820 nm is measured and stored in the memory of the computer Then the sample is placed in the beam and the transmitted light as I_.. intensity at the same values of λ is measured as I_t. The ratio I_t/I_{(λ}) is calculated and displayed on a computer monitor which can then be plotted. The effect of forward scattering on I_t/I_o was estimated from the distance of the photodiode from the scattering suspension and its diameter and found to be > \pm 0.3%. The temperature of the reference material or the colloidal system throughout the experiment is kept constant via a thermal control unit. Fig. 2 shows a schematic diagram of the experimental setup.

Three colloidal systems were studied. The first one was a dispersion of latex particles whose mean particle radius and standard deviation are 0.273 μ m and 0.0041 μ m, respectively. The second system was a bimodal latex suspension obtained by mixing a suspension of particles with radius

Fig. 2 Schematic diagram of the experimental apparatus. L - light source. S - sample holder surrounded by a jacket of flowing water. T - Temperature control bath. CU - cuvette with sample or reference material. G - grating. D - photodiode-array. C - computer. P - plotter.

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0.241 μ m and stardard deviation 0.0025 μ m with a second one for which $\bar{a} =$ 0.595 μ m and $\sigma = 0.027 \,\mu$ m, respectively. The two latex suspensions were mixed in such a way that the number of particles of the first suspension constituted 99.8% of the final suspension. The suspension was diluted such that the volume fraction was smaller than 0.03%. The third system, studied for its high polydispersity and undefined distribution, was a water/silicone oil emulsion of 0.1 v/v%. This volume fraction was chosen to avoid multiple scattering. The emulsion was formed by shaking 0.05 ml distilled deionized water and 50 ml silicone oil (84 mPas) for 1 minute and then ultrasonicating the two phases for 15 minutes. The optical properties of the different materials involved in the experiments are shown in Table 1.

TABLE 1: LIST OF REFRACTIVE INDICES OF WATER, SILICONE OIL AND LATEX AT 25 C.

MATERIAL	REFRACTIVE INDEX
WATER	1.333
SILICONE OIL	1.402
LATEX	1.581

RESULTS AND DISCUSSION

Measured values of I_t/I_o versus λ for the aqueous latex dispersions and the water/silicone oil emulsion are shown in Fig. 3. Assuming a suitable size distribution, theoretical values of $(I_t/I_o)_{theor}$ or $(T_m/T_m)_{n \ theor}$ at two wavelengths, λ_m and λ_n , can be computed using eqs. [2], [10] and [11]. Comparing this to an experimentally measured $(I_t/I_o)_{exp}$ or $(T_m/T_m)_{m \ n \ exp}$ calculated from Fig. 3, one can define the difference between

Fig. 3 Experimentally observed change of I_t/I_o with wavelength for water/silicone oil emulsion, monodisperse latex dispersion and bimodal latex dispersion.



the experimental and the theoretical values of (I_t/I_0) or (T_t/T_1) , Δ , as

$$\Delta = (T_{m}/T_{n})_{exp} - (T_{m}/T_{n})_{theor}$$
[18a]

or

$$\Delta = \left\{ \left(\mathbf{I}_{t} / \mathbf{I}_{o} \right)_{exp} - \left(\mathbf{I}_{t} / \mathbf{I}_{o} \right)_{theor} \right\} (\lambda)$$
[18b]

For other pairs of λ_{n} and λ_{n} in the case of Eq. [18a] or other values of λ in the case of Eq. [18b], the same procedures can be followed and hence other values of Δ can be obtained. The error, ε , resulting from all calculated values of Δ is given by

$$\varepsilon = \sqrt{\Sigma \ \Delta_i^2} \quad . \tag{19}$$

Initially the emulsion droplets were assumed to follow a log normal size distribution. Eqs. [12] and [13] show that there are 4 parameters to consider in choosing the distribution that can best describe the emulsion droplets. These parameters are, \bar{a} , σ , the minimum radius, a_{\min} , and the maximum radius, a_{\max} . For given values of \bar{a} and σ , the choice of a_{\min} and a_{\max} affects the calculated values of the turbidity ratio and the transmitted light intensity. The effect of a_{\min} on the calculated values of (T_m/T_n) and (I_t/I_o) decreases as a_{\min} becomes smaller. This effect vanishes as a_{\min} reaches a certain value. This value of a_{\min} was found to be 0.01 μ m. To generalize the computer program, a much lower value of a_{\min} was chosen in such a way that no underflow errors arise in the computer calculations.

Unfortunately the same could not be done for a_{max} . The reason for this is that, according to the theory, scattering from large particles is much more important than from small ones. Therefore a computer program was developed to integrate the suitable particle size distribution for a given \bar{a} and σ from a_{min} to many different values of a_{max} such that Σn_i^* ranges from 0.98 to 0.999 by an increment of 0.002. Computer results showed that Σn_i^* does not go below 0.98 for the range of a_{max} chosen. The error defined by Eqs. [18] and [19] was calculated for each value of a_{max} and the set $(\bar{a}, \sigma, a_{max})$, which gives the smallest error, was chosen. The same procedures were repeated for other values of \bar{a} and σ and hence another set of $(\bar{a}, \sigma, a_{max})$ was obtained. Among these sets the distribution which best describes the emulsion droplets is the one which give the minimum error.

It was hoped that ε would decrease until a minimum value was reached, beyond which it would increase again. In this case the minimum value of ε would be chosen to represent the emulsion. Instead, the error kept decreasing and no minimum was found. This leads to the conclusion that the emulsion droplets cannot be represented by a log normal distribution. We confirmed this conclusion by implementing Melik and Fogler's method. Their method also indicated that the emulsion cannot be represented by a log normal distribution.

According to Sherman (7) and Li and Fogler (17), when ultrasonic waves are applied at the interface between two liquids, fingers of one liquid penetrate the other liquid and eventually break up into droplets. Upon the break-up process, the main droplets are accompanied by smaller ones called sattelite droplets. This argument suggests that the emulsion might be described by a bimodal distribution. Theoretically, a bimodal distribution

can be formulated by adding two log normal distributions with different proportions of one to the other. Therefore such a distribution has 5 parameters, namely \overline{a}_1 , \overline{a}_2 , σ_1 , σ_2 and x. \overline{a}_1 and σ_1 are the mean radius and the standard deviation of the first log normal distribution, and \overline{a}_2 and σ_2 are the mean radius and the standard deviation of the second distribution, and x is the ratio of droplets in the first distribution and to the total number of droplets..

The theoretical values of (I_t/I_t) were compared to the experimentally measured ones by inputting various values of the above 5 parame-The range of the parameters inputted was made wide enough to ensure ters. that the final result is within this range. The range of the parameters was 0.05 to 0.6 for σ_1 , 0.05 μ m to 1.0 μ m for both \overline{a}_1 and \overline{a}_2 , 0.5 to 1.2 for σ_2 and 0.95 to 1.0 for x. The values of σ_1 , σ_2 , \overline{a}_1 and \overline{a}_2 were incremented by 0.05 and x was incremented by 0.004. The error as calculated from Eqs. [18] and [19] initially decreased and at some point it started to The minimum value of the error indicated that the actual partincrease. icle radius distribution can be best fitted by $(\overline{a}_1, \sigma_1, \overline{a}_2, \sigma_2, x) = (0.23 \pm$ $0.02 \ \mu m$, 0.25 ± 0.05 , $0.30 \pm 0.05 \ \mu m$, 0.85 ± 0.05 , 0.992 ± 0.002). The minimum error calculated from Eqs. [18] and [19] was 0.50 ± 0.04%. A somewhat better result could have been found if a smaller increment had been used, but because of the long computational time the increments mentioned above were deemed sufficient. A comparison between the experimentally measured and the theoretically calculated (I_t/I_p) values can be seen in Fig. 4.

It should be mentioned that besides log normal and bimodal distributions, Gaussian and gamma distributions were also checked. The results

Fig. 4 Comparison between the experimental and theoretical values of (I_t/I_o) for the bimodal latex dispersion and the water/silicone oil emulsion. In the figure the solid lines and the symbols represent the theoretical and experimental values, respectively.


indicated that the emulsion cannot be described by these distributions either.

In interpreting the experimental data for the latex suspension in which the particles have a narrow size distribution, the particle size distribution was assumed to be Gaussian. Eqs. [12] and [13] were reformulated accordingly (see Appendix 2-C). The result obtained by comparing experimentally measured and theoretically calculated turbidity ratios is $(\bar{a},\sigma,a_{\max},\varepsilon) = (0.247 \pm 0.001 \ \mu\text{m}, 0.0041 \pm 0.002 \ \mu\text{m}, 0.262 \pm 0.001 \ \mu\text{m}, 0.0108 \pm 0.0001)$. The comparison with data provided by the supplier is shown in Table 2. The experimentally measured and theoretically calculated values of (T_{μ}/T_{n}) are compared in Table 3. It should be mentioned here that although three turbidity measurements at three wavelengths are required to estimate the particle radius distribution, all the measurements shown in Table 3 were used to obtain better statistical results.

	DISPERSION AND THE UNE	S PROVIDED BY THE S	SUPPLIER.
	DATA PROVIDED		
	BY SUPPLIER	THIS METHOD	* ERROR
a (μm)	0.273	0.247	9.5
σ (µm)	0.0041	0.0040	2.4

TABLE 2: COMPARISON BETWEEN THE EXPERIMENTAL RESULTS FOR LATEX DISPERSION AND THE ONES PROVIDED BY THE SUPPLIER.

The parameters, \bar{a}_1 , σ_1 , \bar{a}_2 , σ_2 and x, for the bimodal latex dispersion were estimated by comparing experimental and theoretical values of (I_t/I_o) . The bimodal distribution for this case was theoretically generated by adding two Gaussian distributions since the suspension was prepared from two narrow size distributions. The minimum error calculated from Eqs. [18] and

[19] indicated that $(\bar{a}_1, \sigma_1, \bar{a}_2, \sigma_2, x) = (0.245 \pm 0.005 \ \mu\text{m}, 0.0025 \pm 0.0005 \ \mu\text{m}, 1.55 \pm 0.05 \ \mu\text{m}, 0.013 \pm 0.008 \ \mu\text{m}, 0.998 \pm 0.0004)$. The value of the error as calculated from Eqs. [18] and [19] is $1.4 \pm 0.4\%$. The comparison between these results and the ones obtained from the supplier is shown in Table 4. The comparison between the experimentally measured and the theoretically calculated (I_t/I_o) can be seen in Fig. 4.

TABLE 3: LIST OF EXPERIMENTALLY MEASURED AND THEORETICALLY CALCULATED VALUES OF (T /T) AT THE WAVELENGTHS INDICATED IN COLUMN 1 FOR THE MONODISPERSE LATEX-WATER SUSPENSION.

λ _ , λ	(T/T) m n exp	(T /T) m n theor	% ERROR
	0.8720	0.8651	0.79
5.80, 0.75	0.7573	0.7474	1.31
0.80, 0.65	0.6422	0.6375	0.73
0.00, 0.00	0.5390	0.5350	0.74
0.00, 0.55	0.4559	0.4469	1.97
n 80. 0.50	0.3771	0.3712	1.56
70. 0.65	0.8480	0.8520	-0.47
0.70, 0.60	0.7118	0.7159	-0.58
0.70, 0.55	0.6021	0.5980	0.68
0.70, 0.50	0.4980	0.4967	0.26
0.60. 0.55	0.8459	0.8353	1.25
0.60, 0.50	0.6997	0.6938	0.84

TABLE 4:	COMPARISON BETWEEN THE EXPERIMENTAL RESULTS FOR	R
	LATEX DISPERSIONS AND THE ONES PROVIDED BY THE	
	SUPPLIER.	

	ā	σ ₁ ā ₂ (μm)	ā_(μm)	°2	x	
					(as prepared)	
SUPPL I ER	0.241	. 0025	1.595	0.024	0.998	
OUR METHOD	0.245 1.6	. 0025 0	1.55 2.8	0.013 52	0.998 0	

COMPARISON WITH OTHER TURBIDIMETRIC METHODS

The method was further tested on data obtained from ref. (9). Gledhill has described a method to determine the particle size distribution by turbidimetry. His method is based on measuring the specific turbidity, $(\tau/\phi)_{\alpha}$ and the logarithmic slope, S, defined as

$$S = - (\partial \ln \tau / \partial \ln \lambda)_{a}$$
, [20]

where τ is the turbidity and ϕ is the volume fraction of the particles. Hence

$$S\tau/\phi = - \left[\partial(\tau/\phi)/\partial \ln\lambda\right]$$
 [21]

Assuming a particle size distribution, $(\tau/\phi)_{o}$ and $(S\tau/\phi)_{o}$ can be theoretically calculated. The particle size distribution can then be obtained by comparing the theoretical values of $(\tau/\phi)_{o}$ and $(S\tau/\phi)_{o}$ with the experimental ones. Our method, which is also based on comparing experimental and theoretical values of the turbidity ratio, eliminates the need for the logarithmic slope or the wavelength exponent which requires very tedious mathematics and a long computation time, especially when the nature of the distribution is not known and different types of distribution are to be tried. Furthermore, our method does not require a knowledge of the volume fraction ϕ .

Data points of τ/ϕ versus λ for dispersion number 4 were read from Fig. 4 in Gledhill's paper. The refractive index of this dispersion is 1.166.

These data were analyzed by our method, assuming a log normal distribution with the result $(\bar{a}, \sigma, a_{max}, \varepsilon) = (0.123 \pm 0.001 \ \mu\text{m}, 0.336 \pm 0.003, 0.347 \pm 0.001 \ \mu\text{m}, 6.3 \pm 0.1\%)$. These results are compared to those of Gledhills's in Table 5.

An F-test on these results (18) shows that there is no real difference between the results obtained by the electron microscope and by this method.

-0.8
13.1
a #4 in ref. (9). distribution as
ر (σ)] }

TABLE 5: COMPARISON BETWEEN THE RESULTS OF GLEDHILL^(a), ELECTRON MICROSCOPY, EM, AND THIS METHOD.

CONCLUDING REMARKS

The particle size distribution of a colloidal system can be estimated by measuring the intensity of the transmitted light at various values of wavelength. For a given particle size distribution and by using the Mie theory for light scattering, several values of turbidity ratio at various wavelengths can be calculated. The selection of the parameters that characterize the particle size distribution that can best describe the colloidal system, is achieved by choosing the distribution for which the difference between several experimental and theoretical values of the turbidity

ratio and the light transmitted intensity is minimum.

The procedure that is based on the turbidity ratio is applicable to samples of unknown volume fraction provided that the system is dilute so that there is no multiple scattering. However, one should be extremely careful in analyzing the data since an infinite number of distributions can give the same turbidity ratio. For this reason we recommend that one uses the procedure that is based on light transmittance data. It is also very important that the refractive indices of the particles and the continuous medium are precisely known. The method is also applicable for the case where particles scatter and absorb light simultaneously. The major advantages of the method are: it is extremely fast and accurate, easy to use and can be applied to highly polydisperse colloidal systems.

Finally, it should be stated that the test which was done on Gledhill's results together with the tests done on the latex suspensions are clear indications of the validity of this method.

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NOMENCLATURE

a _i ,ā	- radius of the particle, m.
a n	- function given by Eq. (5), dimensionless.
A _n	- function given by Eq. (8), dimensionless.
b n	- function given by Eq. (6), dimensionless.
I, I, I, I, I abs o s t	- intensities of the absorbed, incident, scattered and
	transmitted light, respectively, dimensionless.
1	- path length, m.
m	- ratio of the refractive index of the particle to that of
	the continuous media, dimensionless.
n * i	- fractions of particles of class i, dimensionless.
N	- total number of particles per unit volume, m^{-3} .
Р	- probability distribution function.
Q,Q,oext	- scattering, absorption and extinction cross section effici-
	encies, respectively, dimensionless.
x	- fraction, dimensionless.
x	- variable given by Eq. (4), dimensionless.
Y	- variable given by Eq. (7), dimensionless.
Z	- variable given by Eq. (12), dimensionless.
Greek	
æ	- parameter of the gamma distribution.
β	- parameter of the gamma distribution.
ε	- error defined by Eq. (15).
ø	- particle volume fraction, dimensionless.
λ	- wavelength of the light beam, m.

51

- σ standard deviation, its dimension depends on the nature of the distribution.
 - ψ, ψ' Ricatti-Bessel's function and its derivative.
 - ξ, ξ' Hankel's function and its derivative.
 - $\Delta \qquad \text{ the difference between experimental and theoretical values}$ of (I_t/I_o) or (T_m/T_n) defined by Eq. [14], dimensionless.

Script

x - the fraction of one latex dispersion to the whole system.

APPENDIX 2-A

MATHEMATICAL REPRESENTATION OF Q_S IN TERMS OF SPHERICAL BESSEL FUNCTIONS OF ORDER $(n + \frac{1}{2})$. The Mie scattering efficiency coefficient, Q_{g} , is given by

$$Q_{g} = \frac{2}{\chi^{2}} \sum_{n=1}^{\infty} (2n + 1) \left\{ \left| a_{n} \right|^{2} + \left| b_{n} \right|^{2} \right\}, \qquad [1-A]$$

where

$$X = 2\pi a / \lambda_{med} , \qquad [2-A]$$

$$a_{n} = \frac{A_{n}(y)\psi_{n}(X) - m\psi_{n}'(X)}{A_{n}(y)\xi_{n}(X) - m\xi'(X)}, \qquad [3-A]$$

$$b_{n} = \frac{mA_{n}(y)\psi(X) - \psi_{n}'(X)}{mA_{n}(y)\xi_{n}'(X) - \xi_{n}'(X)} , \qquad [4-A]$$

$$A_{n}(y) = \psi_{n}'(y)/\psi_{n}(y)$$
, [5-A]

$$y = mX , \qquad [6-A]$$

$$\psi'_{n}(y) = d\psi_{n}(y)/dy , \qquad [7-A]$$

 $\psi_n(X)$ and $\xi_n(X)$ can be written in terms of the Bessel function of the first kind of order $(n + \frac{1}{2})$ by using the definitions of spherical Bessel functions

$$\psi_{n}(X) = \left(\frac{\pi X}{2}\right)^{1/2} J_{n+1/2}(X) ,$$
 [8-A]

$$\xi_{n}(X) = \left(\frac{\pi X}{2}\right)^{1/2} \left[J_{n+1/2}(X) + (-1)^{n} i J_{-n-1/2}(X)\right], \qquad [9-A]$$

$$\psi_{n}^{*}(X) = \frac{d\psi(X)}{dx} = -\left(\frac{\pi X}{2}\right)^{1/2} \left[J_{-n+1/2}(X) + \frac{n}{x}J_{-n-1/2}\right],$$
 [10-A]

$$\xi'(X) = \frac{d\xi(X)}{dX} = \left(\frac{\pi X}{2}\right)^{1/2} \left\{ J_{n-1/2}(X) - \frac{n}{X} J_{n+1/2}(X) \right\}$$

$$- (-1)^{n} i \left[J_{-n+1/2}(X) + \frac{n}{X} J_{-n-1/2}(X) \right] \qquad [11-A]$$

substitution of Eqs. [8-A]-[10-A] and [11-A] in [3-A] and [4-A] gives (dropping the arguments for simplicity)

$$a_{n} = \frac{\left[\left(\frac{A_{n}}{m} + \frac{n}{X} \right) J_{n+1/2} - J_{n-1/2} \right]}{\left[\left(\frac{A_{n}}{m} + \frac{n}{X} \right) \left(J_{n+1/2} + (-1)^{n} i J_{-n-1/2} \right) \right] - \left[J_{n-1/2} - (-1)^{n} i J_{-n+1/2} \right]},$$
[12-A]

$$b_{n} = \frac{\left[\left(mA_{n} + \frac{n}{X} \right) J_{n+1/2} - J_{n-1/2} \right]}{\left(mA_{n} + \frac{n}{X} \right) \left(J_{n+1/2} + (-1)^{n} i J_{-n-1/2} \right) - \left(J_{n-1/2} - (-1)^{n} i J_{-n+1/2} \right)}.$$
[13-A]

The recurring formula is

$$w_n(X) = \frac{2n-1}{X} w_{n-1}(X) - w_{n-2}(X)$$
, [14-A]

with

ы

$$w_{o}(X) = \sin X - i\cos X = \left(\frac{\pi X}{2}\right)^{1/2} \left[J_{1/2}(X) + i J_{-1/2}(X)\right],$$

$$W_{-1}(X) = \cos X - i \sin X = \left(\frac{\pi X}{2}\right)^{1/2} \left[J_{-1/2}(X) - i J_{1/2}(X)\right].$$

Note that Bessel functions are related to each other by the following formula (Hand Book of Mathematical Functions, pp.390 and 457):

1.
$$J_{n+1}(X) = \frac{2n}{X} J_n(X) - J_{n-1}(X)$$
.
2. $J_n(x) = \left(\frac{\pi}{2X}\right)^{1/2} J_{n+1/2}$.

Therefore

$$w_{1} = \frac{w_{0}}{X} - w_{-1}$$
$$= \sqrt{\frac{\pi X}{2}} \left[\frac{J_{1/2}}{\frac{1}{X}} + i \frac{J_{-1/2}}{\frac{-1}{X}} \right] - \sqrt{\frac{\pi X}{2}} \left[J_{-1/2} - i J_{1/2}(X) \right]$$

Applying property number 1 we can write

$$J_{1/2} = -\frac{1}{X} J_{-1/2} - J_{-3/2} \qquad \left(n = -\frac{1}{2}\right)$$
$$J_{3/2} = \frac{1}{X} J_{1/2} - J_{-1/2} \qquad \left(n = \frac{1}{2}\right)$$

using the above expressions for J and J , w becomes $\frac{1}{1/2}$ and $\frac{1}{3/2}$, $\frac{1}{1}$

$$w_{1} = \left(\frac{\pi X}{X}\right)^{1/2} \left[\frac{J_{1/2}}{X} + i \frac{J_{-1/2}}{X} - J_{-1/2} + i J_{1/2}\right]$$
$$= \left(\frac{\pi X}{2}\right)^{1/2} \left[J_{3/2} + i J_{-3/2}\right],$$

in the same way

$$w_{2} = \left(\frac{\pi X}{2}\right)^{1/2} \left[J_{5/2} - i J_{-5/2}\right] .$$

In general

$$w_{n}(X) = \left(\frac{\pi X}{2}\right)^{1/2} \left[J_{n+1/2}(X) + (-1)^{n} i J_{-n-1/2}(X)\right].$$
 [15-A]

Going back to Eq. [12-A], the numerator contains the terms $J_{n+1/2}$ and $J_{n-1/2}$. By comparing $J_{n+1/2}$ to $w_n(X)$ we can write

$$J_{n+1/2} = R_{e} \left[w_{n}(X) / (\pi X/2)^{1/2} \right]$$
$$J_{n-1/2} = R_{e} \left[w_{n-1}(X) / (\pi X/2)^{1/2} \right]$$

where R indicates the real part of the expression. The denominator is simply $w_n \sqrt{\pi X/2}$ and $w_{n-1} / \sqrt{\pi X/2}$. Therefore the Mie coefficient, $a_n(X)$, can be written as

$$a_{n} = \frac{\begin{pmatrix} A_{n} \\ \overline{m} + \overline{X} \end{pmatrix} R_{e}(w_{n}(X)) - R_{e}(w_{n}(X))}{\begin{pmatrix} A_{n} \\ \overline{m} + \overline{X} \end{pmatrix} w_{n}(X) - w_{n-1}(X)} . \qquad [16-A]$$

In the same way

$$\mathbf{b}_{n} = \frac{(\mathbf{m}A_{n} + \mathbf{n}/\mathbf{X})R_{e}(\mathbf{w}_{n}(\mathbf{X})) - R_{e}(\mathbf{w}_{n-1} + (\mathbf{X}))}{\left(\mathbf{m}A_{n} + \frac{\mathbf{n}}{\mathbf{X}}\right)\mathbf{w}_{n}(\mathbf{X}) - \mathbf{w}_{n-1}(\mathbf{X})}$$
[17-A]

The factor $A_n(y)$ (where y = mX) can be either a real or a complex number depending on the refractive index. The following treatment is valid for both real and complex y

$$A_{n}(y) = \frac{\psi_{n}'(y)}{\psi_{n}(y)} = \frac{-\left(J_{-n+1/2}(y) + \frac{n}{y}J_{-n-1/2}(y)\right)}{J_{n+1/2}(y)} = \frac{J_{n-1/2}}{J_{n+1/2}} - \frac{n}{y} ,$$
[18-A]

let n = n - 1 in [18-A], we can write

$$A_{n-1} = \frac{J_{n-3/2}}{J_{n-1/2}} - \frac{n-1}{y} ,$$

or,

$$A_{n-1} = \frac{\left[(2n - 1)/y \right] J_{n-1/2} - J_{n+1/2}}{J_{n-1/2}} - \frac{n - 1}{y} ,$$

$$A_{n-1} = \frac{n}{y} - \frac{J_{n+1/2}}{J_{n-1/2}} ,$$
[19-A]

combining [19-A] and [18-A] to get

$$A_{n}(y) = -\frac{n}{y} + \left(\frac{n}{y} - A_{n-1}(y)\right)^{-1}, \qquad [20-A]$$

note that $A_{o}(y) = \cot(y)$. [21-A] Therefore the final formulas to be solved are

$$a_{n} = \frac{\left(\frac{A_{n}(y)}{m} + \frac{n}{X}\right)R_{e}(w_{n}(X)) - R_{e}(w_{n-1}(X))}{\left(\frac{A_{n}(y)}{n} + \frac{n}{X}\right)w_{n}(X) - w_{n-1}(X)},$$
[22-A]

$$b_{n} = \frac{\left(mA_{n}(y) + \frac{n}{X}\right) R_{e}(w_{n}(X)) - R(w_{n-1}(X))}{\left(mA_{n}(y) + \frac{n}{X}\right) w_{n}(X) - w_{n-1}(X)},$$
[23-A]

where

$$W_n(x) = \left(\frac{\pi X}{2}\right)^{1/2} \left[J_{n+1/2}(X) + (-1)^n i J_{-n-1/2}(X)\right],$$
 [24-A]

and

$$w_{n-1}(X) = \left(\frac{\pi X}{2}\right)^{1/2} \left[J_{n-1/2}(X) + (-1)^{n-1} i J_{-n+1/2}(X)\right],$$
 [25-A]

$$A_{n}(y) = \left[\frac{n}{y} - A_{n-1}(y)\right]^{-1} - \frac{n}{y}$$
, [26-A]

with

$$A_{o}(y) = \cot(y) . \qquad [27-A]$$

To be able to solve for Q_{g} , the following must be noted:

let

 \bigcirc

$$z = p + iq$$
,

then

$$|z| = \sqrt{p^2 + q^2}$$

and

$$R_{e}(z) = P$$

$$z \text{ conjugate} = \overline{Z} = p - iq.$$

Therefore

$$a_{n} = \frac{\begin{pmatrix} A_{n} \\ \overline{m} + \overline{X} \end{pmatrix} J_{n+1/2} - J_{n-1/2}}{\begin{bmatrix} A_{n} \\ \overline{m} + \overline{X} \end{pmatrix} J_{n+1/2} - J_{n-1/2}} + i(-1)^{n} \begin{bmatrix} A_{n} \\ \overline{m} + \overline{X} \end{bmatrix} J_{-n-1/2} + J_{-n+1/2}}$$

note that $-(-1)^{n-1} = +(-1)^n$.

The next step is to multiply both the numerator and the denominator by the conjugate of the denominator, which is

$$\left[\begin{pmatrix} A \\ \frac{n}{m} + \frac{n}{X} \end{pmatrix} J_{n+1/2} - J_{n-1/2} \right] - i(-1)^n \left[\begin{pmatrix} A \\ \frac{n}{n} + \frac{n}{X} \end{pmatrix} J_{-n-1/2} + J_{-n+1/2} \right]$$

multiply this conjugate with both the numerator and the denominator leads to the following:

1. Numerator

Let
$$A_n/m + n/X = H$$

so

$$(HJ_{n+1/2} - J_{n-1/2}) \{ [HJ_{n+1/2} - J_{n-1/2}] - i(-1)^{n} [HJ_{-n-1/2} + J_{-n+1/2}] \}$$

$$[(HJ_{n+1/2} - J_{n-1/2})(HJ_{n+1/2} - J_{n-1/2})] - i[(-1)^{n}(HJ_{n+1/2} - J_{n-1/2})(HJ_{-n-1/2} + J_{-n+1/2})].$$

2. Denomenator

$$(HJ_{n+1/2} - J_{n-1/2})^2 + [(-1)^n (HJ_{-n-1/2} + J_{-n+1/2})]^2$$

Therefore a becomes

$$a_{n} = \frac{(HJ_{n+1/2} - J_{n-1/2})^{2}}{(HJ_{n+1/2} - J_{n-1/2})^{2} + [(-1)^{n} (HJ_{-n-1/2} + J_{-n+1/2})]}$$

$$- i \frac{(-1)^{n} (HJ_{n+1/2} - J_{n-1/2}) (HJ_{-n-1/2} + J_{-n+1/2})}{(HJ_{n+1/2} - J_{n-1/2})^{2} + [(-1)^{n} (HJ_{-n-1/2} + J_{-n+1/2})]^{2}}$$
[28-A]

then

$$|a_n| = \sqrt{(\text{Real part})^2 + (\text{Imaginary part})^2}$$
. [29-A]

In the same way $|b_n|$ can be found

$$b_{n} = \frac{\left(mA_{n} + \frac{n}{X}\right)J_{n+1/2} - J_{n-1/2}}{\left(mA_{n} + \frac{n}{X}\right)\left(J_{n+1/2} + (-1)^{n}iJ_{-n-1/2}\right) - \left(J_{n-1/2} + i(-1)^{n-1}J_{-n+1/2}\right)}$$

let C = ($mA_n + n/X$) in the above equation to get

$$b_{n} = \frac{CJ_{n+1/2} - J_{n-1/2}}{(CJ_{n+1/2} - J_{n-1/2}) + i ((-1)^{n} CJ_{-n-1/2} - (-1)^{n-1} J_{-n+1/2})},$$

or

$$b_{n} = \frac{CJ_{n+1/2} - J_{n-1/2}}{(CJ_{n+1/2} - J_{n-1/2}) + i(-1)^{n} (CJ_{-n-1/2} + J_{-n+1/2})},$$

multiply both the numerator and the denomenator by the conjugate of the denomenator to get

(1) Numerator

$$(CJ_{n+1/2} - J_{n-1/2}) [(CJ_{n+1/2} - J_{n-1/2}) - i(-1)^{n} (CJ_{-n-1/2} + J_{-n+1/2})],$$

which can be rewritten as

$$(CJ_{n+1/2} - J_{n-1/2})^2 - i[(-1)^n (CJ_{n+1/2} - J_{n-1/2})(CJ_{-n-1/2} + J_{-n+1/2})]$$
.

- Denomenator

$$(CJ_{n+1/2} - J_{n-1/2})^2 + [(-1)^n (CJ_{-n-1/2} + J_{-n+1/2})]^2$$

so b_n becomes

$$b_{n} = \frac{(CJ_{n+1/2} - J_{n-1/2})^{2}}{(CJ_{n+1/2} - J_{n-1/2})^{2} + [(-1)^{n} (CJ_{-n-1/2} + J_{-n+1/2})]^{2}}$$

$$-i \frac{\left[\left(-1\right)^{n} \left(CJ_{n+1/2} - J_{n-1/2}\right) \left(CJ_{-n-1/2} + J_{-n+1/2}\right)\right]}{\left(CJ_{n+1/2} - J_{n-1/2}\right)^{2} + \left[\left(-1\right)^{n} \left(CJ_{-n-1/2} + J_{-n-1/2}\right)\right]^{2}},$$

and $\left|b_{n}\right| = \sqrt{\left(\text{Real part}\right)^{2} + \left(\text{Imaginary part}\right)^{2}}.$

Bessel Functions

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Bessel functions of order n are the solution of the differential equation

$$x^{2} \frac{d^{2}y}{dx^{2}} + \frac{dy}{dx} + (x^{2} - n^{2}) y = 0 .$$

They can be expressed by the following formula:

$$J_{n}(X) = \frac{(X/2)^{n}}{\Gamma(n+1)} - \frac{(X/2)^{n+2}}{1!\Gamma(n+2)} + \frac{(X/2)^{n+4}}{2!\Gamma(n+3)} \dots \text{ for all } n \ge 0$$

in a series form, this equation can be written as

$$J_{n}(X) = \sum_{k=1}^{\infty} \frac{(-1)^{k} (\frac{1}{2} X^{2})^{n+2k}}{k! \Gamma(n+k+1)}$$
 for all $n \ge 0$

where "Г" denotes the Gamma function.

The following equations apply to various Bessel functions:

1.
$$J_{1/2}(X) = \sqrt{2/(\pi X)} \sin X$$

2.
$$J_{-1/2}(X) = \sqrt{2/(\pi X)} \cos X$$

3. $J_{3/2}(X) = \sqrt{2/(\pi X)} \left[\frac{\sin X}{x} - \cos X \right]$

4.
$$J_{-3/2}(X) = \sqrt{2/(\pi X)} \left(\frac{\cos X}{x} + \sin X \right)$$

5. In general

$$J_{n+1}(X) = -\frac{2n}{X} J_n(X) - J_{n-1}(X)$$
.

As mentioned before, the scattering efficiency, Q_{s} is given by

$$Q_{s} = \frac{2}{\chi^{2}} \sum_{n=1}^{\infty} (2n + 1) \{ |a_{n}|^{2} + |b_{n}|^{2} \}$$

where a_n and b_n includes $J_{n+1/2}$, $J_{n-1/2}$, $J_{-n+1/2}$ and $J_{-n-1/2}$. For n = 1these become, respectively, $J_{3/2}$, $J_{1/2}$, $J_{-1/2}$ and $J_{-3/2}$. $J_{5/2}$, $J_{3/2}$, $J_{-3/2}$ and $J_{-5/2}$ for n = 2 and so on for n = 3, 4, etc.

The subroutine MISCAT listed in Appendix 2-B calculates the Bessel functions for n ranging from - 60 to + 60, and spherical Bessel's functions for n rangingfrom - 121/2 to + 121/2. The values for J (the Bessel functions) are used to calculate Q_g .

APPENDIX 2-B

A LISTING OF THE FORTRAN SUBROUTINE MISCAT WHICH WAS USED TO CALCULATE THE SCATTERING EFFICIENCY OF DISPERSED COLLOIDAL PARTICLES

.

SUBROUTINE MISCAT

```
C Subroutine MISCAT to calculate the scattering efficiency,
С
C Q, using the general Mie theory.
С
C In this program needs the following data
С
C RINDEX = ratio of the refractive index of the particles
           to that of the continuous medium.
С
С
C The parameter Z is defined as
С
         = 2.0*PI*RADIUS/WAVE
CΖ
С
C RADIUS = particle radius
         = wavelength of the light in the continuous medium
C WAVE
          = 3.1415927
C PI
С
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION AN(70), BES(130), SPBES(130), F(130)
С
C If the value of Z is > 57 use Van de Hulst equation to
   calculate Q
С
С
        IF(Z.LT.57.) GO TO 7
        RO=2.*Z*(RINDEX-1.0)
        QSCA=2.0-4.0/RO*DSIN(RO)+4.0/(RO*RO)*(1.0-DCOS(RO))
        GO TO 997
С
C In this section Bessel's and spherical Bessel's functions
 C are calculated
 С
      7 F(60)=0.0D0
        F(61) = 1.0D0/Z
        F(62) = 1.0D0/(Z*Z)
        DO 2 N=62,121
        S1=DBLE(N)-61.0D0
        VA=(2.0D0*S1+1.0D0)/Z
        F(N+1) = VA * F(N) - F(N-1)
      2 CONTINUE
        DO 3 K=2,60
        NK=62-K
         S2=1.0D0-DBLE(K)
         VU=(2.0D0*S2+1.0D0)/Z
         F(NK-1) = VU * F(NK) - F(NK+1)
       3 CONTINUE
         L=1
         DO 4 NN=61,121
         VR=((-1.0D0)**NN)*F(NN-L)
         SPBES(NN) = F(NN) * DSIN(Z) + VR * DCOS(Z)
         VX=DSQRT(1.570796326/Z)
```

```
BES (NN) = SPBES (NN) /VX
       L=L+2
     4 CONTINUE
       NU=1
       DO 5 LN=1,60
       LO=61-LN
       XVX=((-1.0D0)**LO)*F(LO+NU)
       SPBES(LO) = F(LO) * DSIN(Z) + XVX * DCOS(Z)
       VF=DSQRT(1.570796326/Z)
       BES(LO)=SPBES(LO)/VF
       NU=NU+2
     5 CONTINUE
C In this section the scattering efficiency is calculated
С
С
       Q=0.0D0
       Y=RINDEX*Z
       AN(1) = DCOS(Y) / DSIN(Y)
       DO 103 J=2,60
       JJ=J-1
       VB=(DBLE(JJ)/Y)-AN(JJ)
       AN(J) = (1.0D0/VB) - (DBLE(JJ)/Y)
       H=(AN(J)/RINDEX)+(DBLE(JJ)/Z)
       ANUM=(H*BES(J+60)-BES(J+59))**2
        PR=(-1.0D0)**JJ
        PX=H*BES(61-J)+BES(62-J)
        ADEN=(PR*PX)**2
        A1=ANUM/(ANUM+ADEN)
        PE=DSQRT (ANUM*ADEN)
        A2=PR*PE/(ANUM+ADEN)
        A=A1*A1+A2*A2
        C=RINDEX*AN(J)+DBLE(JJ)/Z
        BNUM=(C*BES(J+60)-BES(J+59))**2
        PY=C*BES(61-J)+BES(62-J)
        BDEN=(PR*PY)**2
        B1=BNUM/(BNUM+BDEN)
        UX=DSQRT (BNUM*BDEN)
        B2=PR*UX/(BNUM+BDEN)
        B=B1*B1+B2*B2
        Q=Q+(2.D0*DBLE(JJ)+1.D0)*(A+B)
 С
C The value of A and B converges to zero, therefore the
C calculation is terminated when A and B become < 1.0E-10
 С
        IF((A.LE.1.0D-10).AND.(B.LE.1.0D-10)) GO TO 99
    103 CONTINUE
        OSCA = (2.D0/(Z*Z))*Q
    99
    997 CONTINUE
    101 CONTINUE
        RETURN
        END
```

APPENDIX 2-C

MATHEMATIC DERIVATION OF n = AS A FUNCTION OF $a = AND \sigma$ FOR A GAUSSIAN AND A GAMMA DISTRIBUTION FUNCTION

For a Gaussian distribution the probability distribution function is given by

$$P(a) = \frac{1}{\sigma\sqrt{2\pi}} \exp\{-(a - \bar{a})^2/(2\sigma^2)\}.$$
 [1-C)

The fraction of particles between radii a_i and a_{i+1} is given by Eq. [12] with Z_i defined as

$$Z = \frac{a - \overline{a}}{\sigma\sqrt{2}}$$
 [2-C]

For a gamma distribution function the probability distribution function is given by

$$P(a) = 1/\beta^{\alpha} \Gamma(\alpha) a^{\alpha-1} \exp(-\alpha/\beta) , \alpha > 0 , \beta > 0 , \qquad [3-C]$$

 α and β being the distribution parameters; $\Gamma(\alpha)$ is the gamma distribution function. The mean radius and the standard deviation are related to α and β by

$$\overline{a} = \beta(\alpha + 1) , \qquad [4-C]$$

$$\sigma = \beta \sqrt{(\alpha + 1)} \quad . \tag{5-C}$$

If α is a positive integer, the number of particles between a_{i} and a_{i+1} is

$$n_{i}^{*} = - \{ \Sigma [exp(-(a_{i+1}^{\prime}/\beta))(a_{i+1}^{\prime}/\beta)^{\alpha-j} \}$$

• • • • • • • • •

$$- \exp(- (a_{i} / \beta)) (a_{i} / \beta)^{\alpha - j}] (\alpha - j)!) \} . \qquad [6-C)$$

If α is a positive real number the integration of Eq. [3-C] from a to a _ _ i+1 leads to

$$n_{i}^{*} = - \{ \Sigma [exp(-(a_{i+1}^{\beta}))(a_{i+1}^{\beta})^{\alpha-j} - exp(-(a_{i}^{\beta}))(a_{i}^{\beta})^{\alpha-j})] (1/(\alpha - j)!) \}$$

$$\begin{array}{c} a_{i+1} \\ -1/(\beta x \Gamma(x)) \int a^{x} exp(-(a/\beta)) da , \quad [7-C] \\ a_{i} \end{array}$$

where x = 1/2, 1/3, 1/n depending on the value of α . For example if α is 4.5 then x - 1/2 and if α is 19/3 then x = 1/3, etc.

CHAPTER 3

 r^{α}

STABILITY OF WATER IN OIL EMULSIONS IN SIMPLE SHEAR FLOW 1. DETERMINATION OF THE ORTHOKINETIC COALESCENCE EFFICIENCY

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ABSTRACT

A method to estimate the orthokinetic coalescence efficiency of polydisperse droplets in a water/oil emulsion is developed. The method is based on comparing results of experimentally measured and theoretically calculated light transmittance intensities. The experimental values were found by measuring the signal through a water/oil emulsion sheared in a microcouette apparatus. The evolution of the number of droplets with time is followed by solving numerically Smoluchowski's equation. The number of droplets and their radii, as well as the optical properties of the emulsion, were used to calculate the light transmitted intensities as a function of time.

The orthokinetic coalescence efficiency was assumed to be a function of the droplets radius ratio. The model assumes that the orthokinetic coalescence efficiency is maximum when the radius ratio is 1 and that there exists a limiting size, a_c , above which no coalescence occurs. The effect of a_c and hence the surface potential of the droplets on the orthokinetic coalescence efficiency was investigated. A very weak dependence on a_c for a polydisperse system and no dependence for uniform distributions was found. The model contains a parameter C which is expected to be between 1 and 6. For C \leq 6 the coalescence efficiency is found to depend weakly on C.

The effect of the initial droplet size distributions on the orthokinetic coalescence efficiency was examined. For the water in oil emulsions we studied, it was found that the orthokinetic coalescence efficiency is a weak function of the initial droplet size distribution.

INTRODUCTION

Unlike the case of two hard spheres in a simple shear flow, the orthokinetic coalescence efficiency has not been determined for two liquid droplets. The problem arises from the complexity of the equations governing the trajectories of the droplets due to drop deformation and circulation of the fluid inside the droplets.

Curtis and Hocking (1) studied the collision efficiency of a monodisperse polystyrene latex dispersion by looking at the change in the number of particles with time. They used the following equation derived from Smoluchowski's equation to relate the orthokinetic collision efficiency, α_{o} , to the change in the total number of particles

$$\ln(n(t)/N_{o}) = -4\alpha_{o}\phi t/G\pi , \qquad [1]$$

where ϕ is the volume fraction, N_o is the total number of particles at time t = 0 and G is the shear rate. Hazlet and Schechter (2,3) followed a similar way to study the stability of a polydisperse ternary system (a methanol-water-methyl-methacrylate emulsion) sheared between two cylinders with the inner one rotating at a rotational speed Ω and the outer one stationary. They developed a method to determine the collision efficiency from a plot of experimentally measured values of n/N_o versus time which can be related to the experimental variables by

$$\frac{d(n/N_{o})}{dt} (t = 0) = -\frac{G\phi}{W\pi} \left[1 + 3 \exp(-2 \ln^{2}\sigma_{o})\right], \qquad [2]$$

where σ_{o} is the standard deviation of a log normal radius distribution at t = 0 and W is the stability ratio which is the inverse of the collision efficiency (W = $1/\alpha_{o}$).

In these methods, counting the number of particles is the main key of estimating α_{o} . Emulsions which are usually polydisperse systems may contain small droplets below the optical detection limit. When the number of these droplets is very high compared to large droplets (which is usually the case due to their small radius), then this will introduce some error in the estimated values of α_{o} .

Many authors have used light transmittance techniques to study coagulation phenomena. Oster (4) used light transmittance to study polymerization and coagulation of monodisperse particles which were small compared to the wavelength of light (Rayleigh scatterers). He derived the following equation describing the change of turbidity, τ , of coagulating particles

$$\frac{d\tau}{dt} = \frac{8kT}{3\mu_o \rho_p^2} Q_{oxt} w^2 , \qquad [3]$$

where μ_{o} is the viscosity of the continuous medium, ρ_{p} is the density of the particles, Q_{ext} is the light extinction coefficient, k is the Boltzmann constant, T is the absolute temperature and w is the weight fraction of the particles. Timasheff (5) extended Oster's treatment to a region beyond Rayleigh scattering (the Mie scattering region). He described a method for obtaining from turbidimetric measurements an estimate of the rate of particle growth with time as an indication of coagulation based on a theory derived by La Mer et al. (6-8). However as particles grow in size, the

scattering from these particles changes from the Rayleigh to the Mie region. This change can be indicated by a change in the value of an arbitrary exponent which varies from 4.0 (Rayleigh scattering) to - 2.2 (Mie scattering). Therefore to implement the theory of La Mer, measurements of turbidities at various values of wavelengths must be performed to determine the change of the exponent with time. This difficulty was solved by Ottewill and Shaw (9), who investigated the stability of monodisperse latex particles and their coagulation by turbidimetry.

So far all the available methods for estimating the orthokinetic collision efficiency of either solid spherical particles or emulsion droplets in shear flow or for estimating the perikinetic collision efficiency (coagulation of particles in the absence of shear flow) is either based on counting the particles or based on turbidimetry. As a criterion of coagulation, one usually assumes that all the collisions between particles of the same and different radii are equal. Hence the net value of α_0 obtained is an average value of all possible collision efficiencies between the colliding particles.

In this chapter a method based on measuring light transmittance intensity through water/oil emulsions as a function of time is described. We assume that α_0 is a function of the radius ratio of the colliding droplets. This dependence will be discussed later in the section that deals with the method for estimating the orthokinetic coalescence efficiency. The orthokinetic coalescence efficiency is estimated from a direct comparison of measured and calculated values of the light transmittance intensities. Theoretical calculations of the light

transmittance intensities with time were made possible by evaluating the change in the number of droplets by numerically solving Smoluchowski's equation by a fourth order Runga-Kutta integration method (10). This first, light transmittance is extremely method has several advantages: sensitive to any changes in the size distribution of the droplets and, second, it is sensitive to all available sizes of the droplets. This eliminates the problem associated with the minimum size that cannot be seen under the microscope, which the methods that are based on counting the number of droplets cannot avoid. Furthermore, this method eliminates the difficulties that are present in counting the number of droplets in the emulsion and, finally, the measurements are continuous and there is no need to withdraw a sample from the emulsion for analysis under the microscope. On the other hand, the disadvantage of this method is that it can only be applied to systems where the continuous phase is transparent.

THEORETICAL ANALYSIS

Emulsions are thermodynamically unstable systems. Suspended droplets tend to coalesce to form bigger droplets which sediment or cream, depending on the density difference between the dispersed and the continuous phases. The rate at which these droplets coalesce is related to the different forces acting on them. These forces can be a gravitational force, F_g , a Brownian force, F_b , a van der Waals attraction force, F_a , repulsive forces due to the interaction of the electrical double layers around the droplets, F_r , and external forces, F_{ext} , such as hydrodynamic forces, forces due to the presence of magnetic or electrical fields, etc. In mathematical form,

the net force, F_{net} , can be expressed as

$$F_{net} = F_{b} + F_{f} + F_{f} + F_{ext} = 0 .$$
[4]

If the droplets are neutrally buoyant and Brownian motion is negligible, which is true for media of high viscosity, then $F_g + F_b \cong 0$, in which case Eq. [4] reduces to

$$F_{net} = F_a + F_r + F_{ext} = 0 .$$
 [5]

The first attempt to describe the rate at which droplets coalesce was made by Smoluchowski (11). Assuming that the hydrodynamic interaction and the colloidal forces acting on the droplets are negligible except when they make contact, he derived the following equation for the rate of coalescence of a monodisperse colloidal system of spheres of radius a subjected to a simple shear flow of gradient G (12),

$$\frac{dn}{dt} = -\frac{16}{3} Gn^2 a^3 , \qquad [6]$$

where n is the total number of particles per unit volume and t is the time. The minus sign in front of the term on the right hand side of Eq. [6] is to indicate that the number of particles decreases with time.

During a collision between two particles, the particles experience the presence of hydrodynamic and colloidal forces that might exist, e.g. repulsion or attraction forces. Taking these forces into account, van de Ven and Mason (13) corrected Eq. [6] by introducing a factor they called the

orthokinetic coalescence efficiency, α_{o} . Eq. [6] then takes the form

$$\frac{\mathrm{dn}}{\mathrm{dt}} = -\frac{16}{3} \operatorname{Gn}^2 a^3 \alpha_{o} .$$
^[7]

From Eqs. [6] and [7] the orthokinetic coalescence efficiency represents the ratio of the actual coalescence rate to Smoluchowski's coalescence rate.

In general, colloidal systems are polydisperse and one can divide the particles into classes, each of a certain radius a_i and a concentration n_i . The rate of change of n_i can be written as a difference between a production term and a depletion term, or

$$\frac{dn_{i}}{dt} = \frac{4}{3} G \left[\frac{1}{2} \sum_{\substack{j \ k = i \\ j \neq k = i}} n_{j \ k} (a_{k} + a_{j})^{3} \alpha_{o, jk} - n_{i} \sum_{j} (a_{i} + a_{j})^{3} n_{j} \alpha_{o, ij} \right]$$
[8]

where the first term on the right hand side of Eq. [8] represents the production of n_i due to coalescence of smaller sized droplets giving rise to n_i , and the second term represents the depletion of n_i due to its coalescence with itself and with other droplets.

The orthokinetic coalescence efficiency, $\alpha_{o,mn}$ is a function of many parameters such as the viscosity, μ_o , and the dielectric constant, ε , of the continuous medium, the surface potential of the particles, ψ_p , the Hamaker constant of the system, A, the radii of the particles, the shear rate G and the interfacial tension, γ . In mathematical form α_o can be expressed as
$$\alpha_{r} = f(\varepsilon, \mu_{r}, \psi_{r}, \gamma, A, a_{r}, a_{r}, G) . \qquad [9]$$

For a specific system the physical properties are constant and, furthermore, if the applied shear rate is constant then one can write Eq. [9] as

$$\alpha = \text{const. } f(a_1, a_1) .$$
 [10]

Theoretical and experimental studies on coagulation of solid spherical particles in shear flow (14-16) have shown that coagulation between two particles of equal radius (homocoagulation) is favored over coagulation between two unequal radius spheres (heterocoagulation) except under specific conditions (17). The reason can be explained as follows. In the absence of interparticle interactions, the minimum distance (the gap width between a particle in simple shear flow located on a limiting trajectory and the central particle (see Fig. 1)) to which two particles can approach each other is a strong function of the radius ratio (18-21). This suggests that the coalescence efficiency is maximum when the two droplets are of equal radii or the radius ratio is 1.0 and decreases as the radius ratio deviates from 1.0. Van de Ven and Mason (13) showed that for a suspension of monodisperse colloidal particles with constant surface potential, the orthokinetic collision efficiency decreases as the radius of the particles increases and at a critical value of the radius, the orthokinetic collision efficiency suddenly drops to 0. Thus, based on the above discussion, we assume the following dependence of α_{0} on the radius ratio $q_{ij} (= a_{i}/a_{j})$

Fig. 1 Trajectories of two spheres of radii a_1 and a_2 in simple shear flow. The central particle is located at the center of a Cartesian coordinate system. The flow is characterized by open trajectories and closed trajectories, separated by limiting trajectories. In the absence of colloidal forces between the particles, the minimum distance d_{min} , particle a_2 can approach a_1 is defined as the minimum distance between a particle on a limiting trajectory in the equatorial plane and the reference particle.



$$\alpha_{o} = \alpha_{c} \left\{ \begin{bmatrix} 4q_{ij} \\ (1 + q_{ij})^{2} \end{bmatrix}^{c} , a < a_{c} \\ \alpha_{o} = 0 , a > a_{c} \end{bmatrix}$$
[11]

where α_c is the orthokinetic coalescence efficiency coefficient which is a function of G, ε_o , μ_o , ψ_o , a_c and t. C is a constant and a_c is a critical radius above which α_c is 0. Fig. 2 depicts the dependence of α_o on q_{ij} calculated from Eq. [11] for various values of the constant C and for $a_c = 2.0 \ \mu\text{m}$. Fig. 2 shows that values of C ranging between 1 and 6 look the most reasonable since one expects a change over from low to high values of α_o when $q_{ij} = \frac{1}{2}$. The effect of the value of C on α_c will be discussed in later sections.

We define the following dimensionless variables

 $2\eta \in I$

$$\mathbf{n}_{i}^{*} = \mathbf{n}_{i} / \mathbf{N}_{o} , \qquad [12]$$

$$a^* = a / \overline{a}$$
, [13]

$$t^* = \frac{16}{3} GN_o \bar{a}^3 \alpha_c t$$
, [14]

$$q_{ij} = a_i / a_j, \qquad [15]$$

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where N_o is the total number of particles per unit volume at t = 0 and \overline{a} is the mean radius of the particles. In dimensionless form and for a value of C = 1.0, Eq. [8] becomes Fig. 2 The dependence of α_0/α_c on q_{ij} for different values of the constant C as given by Eqs. [11]. For values of $q_{ij} > 1$ the curve is symmetric and $q_{ij} = 1/q_{ij}$ can be used.

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$$\frac{dn_{i}}{dt^{*}} = \frac{1}{2} \sum_{\substack{j \ k \\ j+k=1}} n_{k}^{*} n_{j}^{*} (1+q_{jk}) q_{jk} a^{*^{3}} - n_{i}^{*} \sum_{j} n_{j}^{*} (1+q_{ij}) q_{ij} a^{*^{3}} .$$
 [16]

A list of the FORTRAN subroutine that was used to integrate Eq. [8] or Eq. [16] (COALESCE) is given in Appendix 3-A.

A METHOD FOR ESTIMATING THE ORTHOKINETIC COALESCENCE EFFICIENCY

Let I_o be the incident light intensity passing through the emulsion between two plates a distance *I* apart. I_o will undergo some extinction due to scattering and absorbing of some of its intensity by the emulsion droplets. The rest will be transmitted. If the absorbance is negligible then the transmitted I_t and the incident light intensities are related by the following equation (22):

$$I_{t} / I_{o} = \exp \left[-\pi l N_{o} \sum_{i=1}^{\infty} n_{i}^{*} Q_{s,i} a_{i}^{2} \right], \qquad [17]$$

where $Q_{s,i}$ is the scattering cross section which is a function of the radius of the droplets, the ratio of the refractive index of the droplets to that of the continuous medium and the wavelength of the incident light beam (23). The dependence of $Q_{s,i}$ on these parameters is given by (24)

$$Q_{g} = (2/X^{2}) \sum_{n=1}^{\infty} (2n+1) \{ |a_{n}|^{2} + |b_{n}|^{2} \}, \qquad [18]$$

where

$$X = 2\pi a / \lambda_{med} , \qquad [19]$$

$$a_{n} = \frac{A_{n}(y)\psi(X) - m\psi_{n}'(X)}{A_{n}(y)\xi(X) - m\xi_{n}'(y)},$$
[20]

and

$$b_{n} = \frac{mA_{n}(y)\psi_{n}(X) - \psi_{n}'(X)}{mA_{n}(y)\xi_{n}(X) - \xi_{n}'(X)}, \qquad [21]$$

with

$$y = mX$$
, [22]

and

$$A_{n}(y) = \psi'_{n}(y)/\psi_{n}(y)$$
, [23]

 ψ_n being Ricatti-Bessel's function and ξ_n is related to Hankel's function of the second order. The prime denotes the first derivative with respect to the argument. λ_{med} is the wavelength of the incident light in the medium which is equal to λ/n_{med} , n_{med} being the refractive index of the continuous medium. The dependence of Q_g on X for different values of m is given in Chapter 2.

The method is based on measuring the change in light transmittance intensity experimentally, $(I_t/I_o)_{exp}$. This is compared to calculated values of $(I_t/I_o)_{cal}$ from Eq. [17]. Accordingly, the calculated values of $(I_t/I_o)_{cal}$ as a function of time required knowledge of the change of n_i^* with time. Given the initial droplet radius distribution of the emulsion, n_i^* , the distribution at any time can be calculated by solving Eq. [16]. At

Fig. 3 Illustration of the method used to estimate the orthokinetic collision efficiency. At any time t*, the value of t at which $(I_t/I_o)_{exp} = (I_t/I_o)_{cal}$ can be read from which α_c can be estimated.



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any time t, the value of t* at which $(I_t/I_o)_{cal} = (I_t/I_o)_{exp}$ is found from a figure like the one shown schematically in Fig. 3. Since t* = $16N_oa^3G\alpha_ct/3$ then the value of α_c can be estimated.

The procedure used to estimate the orthokinetic coalescence efficiency discussed in the previous paragraph, can be summarized as follows:

- 1. Eq. [16] is solved numerically from which n_i^* at any dimensionless time t* is known.
- 2. Knowing n_i^* values of (I_t/I_o) at any dimensionless time t* can also be computed from Eq. [17].
- 3. At any dimensionless time t*, the real time t at which $(I_t/I_o)_{cal} = (I_t/I_o)_{exp}$ can be read from a figure like Fig. 3.
- 4. The orthokinetic coalescence efficiency coefficient, α_{c} , is then estimated from the following equation:

$$\alpha_{c} = \frac{3t^{*}}{16GN_{a}\overline{a}^{3}t} , t \neq 0.$$
 [24]

The parameters G, N_{o} and \overline{a} occurring in Eq. [24] are known from the initial experimental conditions.

Eq. [24] is only applicable at t > 0. To estimate the value of α_c at t = 0 the following procedure was followed: taking the derivative of Eq. [17] with respect to t and evaluating the result at t = 0 yields (see Appendix 3-B)

$$\frac{d(I_{t}/I_{o})}{dt} (t = 0) = - (16/3)GN_{o}^{2}l\alpha_{c}\pi\bar{a}^{-3}(I_{t}/I_{o})_{t=0} \sum_{i=1}^{\infty} [Q_{s,i}a_{i}^{2}(dn_{i}^{*}/dt^{*})]$$
[25]

The sum on the right hand side of Eq. [25] can be calculated numerically. It should be noted that Eq. [25] is valid not only at t = 0 but also at any t > 0.

Another way to estimate α_c at t = 0 is to extrapolate the curve that results from plotting α_c versus t or t* to t = 0.

EXPERIMENTAL DETAILS

Experimental Apparatus

The experimental setup is a microcouette apparatus that consists of two parallel plates. The plates are made parallel to an accuracy within \pm 20 μ m which corresponds to 1.0% of the gap width between the two plates. This is achieved by means of a dial indicator whose accuracy is 2.5 μ m. The plates are made of special optical glass. The diameters of the top and bottom plates are 15.2 cm and 15.8 cm, respectively, and the thickness is 4.0 mm. The lower plate can rotate clockwise or counter-clockwise with an adjustable rotational speed by means of a motor. The upper plate is stationary, yet it can move up or down to achieve the required gap width between the two plates. To avoid any instability at the onset of rotation and to achieve constant rotational speed right from the beginning, the motor is connected to a clutch which prevents the bottom plate from rotation until the desired rotational speed is reached.

A He-Ne laser (Uniphase, model 1105P, serial number 202052) of 633 nm wavelength passing through a pinhole (3.2 mm) falls on the emulsion contained between the two plates. The intensity of the transmitted light is measured by a photodiode from which the signal is sent to a power meter

(Coherent Radiation Laboratory model 212). the output of the power meter is received by a data acquisition system (Fluke 525033, 8500 A digital multimeter) and then by a microcomputer for storage and data handling. The fluctuation of the laser light is < 0.4%. A schematic diagram of the experimental apparatus is portrayed in Fig. 4. A photograph of the experimental setup can be seen in Appendix 3-C.

Prior to the light transmittance measurements through the emulsion, 100% light transmittance, I_o , was measured. 50 ml of the continuous medium (this quantity is equal to the amount of the emulsion being sheared) is placed between the two plates and the intensity of the light passing through is measured. The emulsion is then placed in the cell and the transmitted light through the emulsion is recorded. Due to the presence of the glass plates, the transmittance through the continuous medium and the emulsion has to be corrected to obtain I_o and I_t , respectively. The correction due to the presence of the glass plates is done as follows (see Fig. 5): the experimental values of $(I_t/I_o)_{exp}$ that are needed to be compared to the theoretical values of $(I_t/I_o)_{cal}$ are the values of I_t measured at position 3, Fig. 5b, and the value I_o measured at position 2, Fig. 5a.

From Fig. 5a the attenuation due to the presence of the upper plate and the lower plate is equal to $(I_1 - I_{4,a})$, where I_1 and $I_{4,a}$ are both measurable quantities. Assuming that the two plates are identical, then the attenuation due to each plate is equal to $(I_1 - I_{4,a})/2$. $I_o = I_2$ is the intensity of the light at position 2 which is equal to $I_1 - (I_1 - I_{4,a})/2$. From Fig. 5b the transmitted light through the emulsion which is equal to $(I_{4,b} - I_{5,3})$ where $I_{5,3}$ is the amount of the scattered light due to the air-glass and glass-oil interfaces at position 3. Then $(I_1/I_o)_{exp} =$

Fig. 4 Schematic diagram of the experimental apparatus used in this study. L is a laser light source, P is a pinhole, M is a mirror, MC is a microcouette apparatus which consists of two plates. The upper one is stationary and the lower one rotates at an adjustable rotational velocity Ω . The plates are separated by a distance I and the distance from the center of the plates to where the laser passes through the cell is r. PH is a photodiode, PM is a photomultiplier, DAS is a data acquisition system and PC is a personal computer.



- Fig. 5 Illustration of the procedure used to correct for the scattering due to the glass/oil and glass/air interfaces.
 - (a) The case when pure silicone oil is present.

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(b) The case when the emulsion is present in the cell.









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 $[2.0(I_{4,b} - I_{s,3})/(I_1 + I_{4,a})]$ is the quantity to be compared to $(I_t/I_o)_{cal}$. I_1 , $I_{4,a}$ and $I_{4,b}$ are all measurable quantities and $I_{s,3}$ can be computed from knowing both I_1 and $I_{4,a}$.

The effect of forward scattering on $(I_t/I_o)_{exp}$ was estimated from the aperture of the photodiode and its distance from the scattering sample. It was found that this effect is less than 1.0%, which is negligible compared to the signal of the transmitted light.

The applied shear rate is calculated by solving the equation of motion and the continuity equation for this geometry (Fig. 6).

$$\left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (rv_{\theta})\right)\right] + \frac{\partial^2 v_{\theta}}{\partial z^2} = 0 . \qquad [27]$$

$$\frac{\partial v_{\theta}}{\partial \theta} = 0 \quad .$$
 [28]

The solution of these equations employing the appropriate boundary conditions and for Re = $\rho_o v_{\theta} l/\mu_o << 1.0$ (see Appendix 3-D) results in

$$G = \frac{2\pi\Omega r}{l} .$$
 [29]

where Ω is the rotational velocity, r is the radial distance from the center of the plates at which the light falls and *l* is the gap width between the two plates. In the experiments performed *l* was 2.3 mm. The value of r is chosen large enough such that $l/r \ll 1.0$, yet smaller than the radius of the plates to avoid end effect problems.

Fig. 6 The flow pattern in the system of two plates where the upper one is stationary and the lower one rotates at an angular velocity Ω for the case where Re = $\rho_{o} v_{\theta} l/\mu_{o} \ll 1.0$.





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Material

The emulsion tested is a water/silicone oil emulsion of 0.2 v/v%. This concentration was chosen to avoid multiple scattering and many-body interactions. According to Fogler et al. (25), 0.2 v/v% for their system was the limit beyond which multiple scattering would take place. The refractive index difference of the system they used (m = 1.16) is larger than water/silicone oil (m = 0.95), therefore the concentration chosen to study this system is far below the concentration at which multiple scattering occurs. Water is distilled, deionized and filtered through a 0.22 μ m filter. The oil is Dow Corning 200 silicone oil of 100.0 cs (viscosity = 97 mPas).

The emulsions were prepared by adding 50.0 ml of silicone oil to 0.1 ml water and then mechanically shaken (Burrell PGH.PA mechanical shaker) for 1 minute. The two phases are then ultrasonicated for 15 minutes (Branson ultrasonic cleaner B-220). The viscosity was measured by a Bohlin rheometer VOR system and the interfacial tension (28 mN/m) measurement was done by the pendent drop method (26). All the measurements were done at room temperature ($22^{\circ}C \pm 1$).

Cleaning of the Glassware

Great care should be taken in cleaning the glassware. Earlier studies in this lab showed that if proper cleaning procedures are not followed a lyophilic or lyophobic medium on the wall of the flask in which the emulsion is prepared may be created. Therefore the following cleaning procedures were followed to ensure that the wall of the flask has the same nature in all the experiments performed. The flask is washed first with a

cleaning solution and then ultrasonicated with a new quantity of cleaning solution for a few minutes. The flask is then washed and filled with a chromic acid for a few hours. The chromic acid is washed off and then the flask is ultrasonicated for a few minutes and finally washed with distilled water.

RESULTS AND DISCUSSION

Fig. 7 shows experimentally measured changes in light transmitted intensity versus time for a water/silicone oil emulsion sheared at 10 s⁻¹. The change in the signal is only due to orthokinetic coagulation, i.e. due to the presence of shear. To check this claim, I_t/I_o as a function of time in the absence of rotation or at G = 0.0 was studied and the result is portrayed in Fig. 8. It can be seen from Fig. 8 that perikinetic coagulation is negligible compared to an orthokinetic one. This can also be seen by estimating the Peclet number, Pe, for this system, which is a measure of the importance of orthokinetic coagulation to perikinetic coagulation, i.e.

$$Pe = \frac{Orthokinetic \ coagulation \ rate}{Perikinetic \ coagulation \ rate} > 53 \ .$$
[30]

The orthokinetic and perikinetic coagulation rates were estimated from Smoluchowski's kinetics using a mean particle radius of 0.5 μ m.

Eq. [16] was solved numerically. The dependence of α_0 on the droplet radius ratio was taken as given by Eqs. [11] with a value of C = 1.0. The integration of Eq. [16] was done using a constant size integration step. The integration step was chosen as follows: a certain integration step,

Fig. 7 Experimentally measured I_t/I_o versus time for water/silicone oil emulsion sheared at 10 s⁻¹.

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Fig. 8 Experimentally measured I_t/I_o versus time for water/silicone oil emulsion in the absence of shear (G = 0.0).

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t₁, was chosen and the light transmitted intensities as a function of time were calculated. A smaller integration step, say t₂, is then chosen and the light transmittance intensities were again calculated. At any time t, if the percent difference between the light intensities calculated at the two integration steps, Δ, is greater than 0.01% (i.e. $\Delta = |[(I_t/I_o)_{t1} - (I_t/I_o)_{t2}]/(I_t/I_o)_{t1}]| \times 100)$, then a smaller integration step is chosen until the percent difference is < 0.01%. In fact, the integration step used in these calculations yields a value of Δ much smaller than 0.01%.

The initial droplet radius distribution was divided into classes such that the volume of class i is made of i number of primary particles whose volume is V_0 , i.e. $V_1 = iV_0$. Therefore the radius of class i is related to a by this formula;

$$a_i = (i)^{1/3} a_o$$
 [31]

If a_{o} is chosen to be 0.1 μ m and if a_{c} is 2.0 μ m then, according to Eq. [31], the distribution should be divided to 16000 classes. To solve Smoluchowski's equation where the number of classes is 16000 takes a huge memory and a very long computation time. Thus we expand the size of each class by rewriting Eq. [31] in this form;

$$a_{i} = (xi)^{1/3} a_{o},$$
 [32]

where x is an arbitrary number > 1. Eq. [32] says that the classes are $(x)^{1/3}$ bigger than the size of the class results from using Eq. [31]. In other words, a in the case of Eq. [32] is $(x)^{1/3}$ larger than a in the

case of Eq. [31]. The value of x = 10 was chosen in the integration of Eq. [16]. The effect of x on the accuracy of the integration was tested by solving Eq. [16] using x = 5. The difference between the results obtained at x = 10 and those obtained at x = 5 varied only by < 1%. This tolerance is acceptable when the savings in the computation time are considered.

The solution of Eq. [16] requires that the initial droplet radius distribution be known. The initial droplet radius distribution was determined by the method described in Chapter 2. The results showed that the initial droplet radius distribution can be best fit by a bimodal distribution with the following parameters: $(\overline{a}_1, \sigma_1, \overline{a}_2, \sigma_2, x) = (0.23 \ \mu m, 0.25, 0.3$ μ m, 0.85, 0.992). The bimodal distribution was theoretically formulated by adding two log normal distributions whose mean radii and standard deviations are \overline{a}_1 , \overline{a}_2 and σ_1 and σ_2 , respectively. The two log normal distributions were added such that the number of droplets that belong to the first log normal distribution constitute 99.2% of the total number of droplets. It should be mentioned here that although all the experimental conditions were kept similar (same silicone oil, equal sonification time, etc.), in spite of this we did not succeed in preparing emulsions with identical initial droplet radius distributions because of the random nature of the breakage of the interface between the water and the oil (27-29). Therefore the above distribution represents an average droplet radius distribution. We shall see in the following section that the orthokinetic coalescence efficiency, for some typical particle radius range, is a rather weak function of the initial droplet radius distribution. Thus, although an identical initial droplet radius distribution was impossible to prepare, the radii of all the emulsions prepared fall within the same range. This was

confirmed by looking at the droplets under the microscope for different emulsions where it was found that the radius of the largest droplets ranged between 6 and 7 μ m.

Preliminary calculations of α_{o} for different initial log normal radius distributions showed that, at least for the system under consideration, α_{o} is a rather weak function of the initial distribution. Hence we assume that the orthokinetic coalescence efficiency is independent of the initial droplet radius distribution. Proof of this assumption will be discussed in detail below, but first we will show the results obtained for α_{c} using the parameters of the bimodal distribution mentioned above. Fig. 9 shows α_{c} plotted versus the dimensionless number Gt. Comparing these results to different log normal distributions which have the same range of droplet sizes shows that the above assumption is valid.

The ratio I_t/I_o for all the experiments performed (see Chapter 4) ranges between 0.23 to 0.32. Therefore theoretical values of I_t/I_o for many log normal radius distributions of a wide range of mean radius, \bar{a} , and standard deviation, σ , and having a maximum radius of 6.5 μ m, were calculated. To expand the range of possible log normal distributions, all the distributions which gave I_t/I_o between 0.2 and 0.4 where chosen for further analysis of α_o . The range of \bar{a} and σ tried is 0.01-1.0 with an increment of 0.01. Values of \bar{a} and σ beyond this range do not give calculated values of I_t/I_o between 0.2 and 0.4. A plot of σ versus \bar{a} for the distributions which give I_t/I_o between 0.2 and 0.4 is shown in Fig. 10.

If the proposed independence of α_{o} on the initial distribution is correct, then a plot of α_{o} versus Gt should be independent of the distributions $(\bar{a},\sigma) = (0.34 \ \mu\text{m}, 0.01), (0.57 \ \mu\text{m}, 0.01), (0.01 \ \mu\text{m}, 0.70)$ and $(0.3 \ \mu\text{m}, 0.70)$

Fig. 9 A plot of α_c versus the dimensionless number Gt for water/silicone oil emulsion sheared at 10.0 s⁻¹. The value of the critical radius, a_c , above which $\alpha_o = 0.0$ is 2.0 μ m. \bullet , o, Δ and \blacktriangle correspond to $(\overline{a}, \sigma) = (0.34, 0.01), (0.57, 0.01), (0.11, 0.70)$ and (0.30, 0.35), respectively. The curve shown by \Box is the result obtained for a bimodal distribution.



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0.35), which correspond to points a, b, c and d, respectively, in Fig. 10. Moreover, if the calculated values of α_0 for the distributions indicated by a, b, c and d in Fig. 10 are close within an order of magnitude then the actual radius distribution will give values of α_0 similar to the values of α_0 estimated for these distributions. The results of the above-mentioned distributions compared to the results of the actual one are compared in Fig. 9. It can be clearly seen that α_c is a weak function of the initial droplet radius distribution.

 α_{c} was also estimated for G = 199 1/s for the distributions mentioned above and the results are shown in Fig. 11 where the weak dependence of α_{c} on the initial droplet radius distribution can also be noticed.

Preparing a number of emulsions and measuring I_t/I_o versus T for each emulsion, the value of I_t/I_o versus t were found to be reproducible by about 4%. This affects the estimated values of α_c by about 20%.

Here we would like to expand more on the statement that α_c is a weak function of the initial droplet radius distribution. From Fig. 9, and at Gt = 0, α_c is equals 0.22, 0.18 and 0.12 for the distributions $(\bar{a},\sigma) =$ (0.11, 0.7), (0.34, 0.01) and (0.57, 0.01), respectively. This means that among 100 collisions, 22, 18 and 12 were successful or led to coalescence. In other words, $\alpha_c = 0.17 \pm 0.05$ which corresponds to approximately 29% error. At first sight this appears to be a large error, but one should bear in mind that these points represent the most extreme cases. If a narrower range for I_t/I_o and hence the distribution is used, a much smaller error in α_c will be obtained. For example, comparing the above average value of α_c to the one obtained for the actual bimodal distribution (0.19), or to the one obtained for point d (0.16), shows that the error is approxi-

Fig. 10 A plot of standard deviation, σ , versus the mean radius, \overline{a} , for log normal distributions whose maximum radius is 6.5 μ m and which give a range of I_t/I_o between 0.2 and 0.4. Points a, b, c and d correspond to $(\overline{a}, \sigma) = (0.34, 0.01), (0.57, 0.01), (0.11, 0.70)$ and (0.3, 0.35), respectively.



Mean Radius, \overline{a} (μ m)

Standard Deviation, σ

Fig. 11 A plot of α_c versus the dimensionless number Gt for water/silicone oil emulsion sheared at 199 s⁻¹. The value of the critical radius, a_c above which $\alpha_o = 0$ is 2.0 μ m. $\blacklozenge, \bigstar, \lor, \lor$ and ∇ correspond to $(\overline{a}, \sigma) = (0.34, 0.01), (0.57, 0.01), (0.11, 0.71)$ and (0.3, 0.35), respectively. The curve shown by \blacksquare corresponds to the results obtained for the bimodal distribution.


mately 8%. These results clearly delineate the weak dependence of α_c on the initial droplet radius distribution. Since the value for the bimodal distribution is the most accurate one, we estimate that $\alpha_c = 0.19 \pm 0.03$.

Effect of a_c on α_c

Eq. [16] was solved for the cases where a_c is 1.5 μ m and 2.5 μ m. For solid particles in simple shear flow, α_o drops to 0 after $a_c = 1.5 \mu$ m and 2.5 μ m if their surface potentials are 75 mV and 43 mV, respectively, (13). We believe that emulsion droplets behave qualitatively in a similar manner. Furthermore, this range of a_c represents a wide range of surface potentials which many colloidal particles have.

A plot of α_c versus Gt for the earlier-mentioned initial droplet radius distributions is shown in Fig. 12. For the distributions $(\bar{a},\sigma) =$ (0.34, 0.2) and (0.57, 0.01) the results of α_c are identical, which is not surprising because the distributions are highly uniform. For the distribution $(\bar{a},\sigma) = (0.11, 0.7)$ the dependence of α_c on a_c is very weak and, on average, does not exceed $\pm 4\%$. It should be mentioned that this dependence on a_c becomes more important as the polydispersity increases.

In the previous figures (Figs. 9, 11 and 12), a decrease in the value of α_c with time can be noticed. As coalescence proceeds, the emulsion droplets grow in radius and thus they can be more readily deformed (since the capillary number increases, Ca = Ga μ/γ , which is a measure of the shear forces to the surface tension forces). Deformation has a considerable effect on the coalescence efficiency. It is lower when the droplets are more deformable (see Chapter 4). Another reason for the slight decrease in α_c , perhaps, is the migration of some impurities that may exist in the oil

Fig. 12 A plot of α_c versus the dimensionless number Gt for water/silicone oil emulsions of a log normal distribution $(\bar{a}, \sigma) = (0.34, 0.01), (0.57, 0.01)$ and (0.11, 0.70) and having a maximum size of 6.5 μ m sheared at 199 s⁻¹ for the cases where a_c is 1.5, 2.0 and 2.5 μ m. \blacksquare and ∇ are for the cases where $(\bar{a}, \sigma) = (0.34, 0.01)$ and (0.57, 0.01), respectively, where no dependence of α_c on a_c was found. , ∇ and are for $(\bar{a}, \sigma) = (0.11, 0.70)$ for $a_c = 1.5, 2.0$ and 2.5 μ m, respectively, where dependence within $\pm 2\%$ of α_c on a_c can be observed.



phase to the water oil interface. These impurities lower the interfacial tension as well as the surface potential. The decrease in the interfacial tension makes the emulsion droplets more deformable and hence decreases the value of α_c with time.

Effect of the Value of C on α_{c}

The effect of the value of the constant C on α_c was tested by solving Smoluchowski's equation (Eq. [8]) written in dimensionless form for different values of C. As the value of C increases the dependence of α_c on q_{ij} , as can be seen from Fig. 2, becomes more symmetric around $q_{ij} = 1$. Fig. 13 shows calculated values of α_c versus C at t* = 0 for values of C ranging between 0 and 100 for water/silicone oil emulsion sheared at G = 10 s⁻¹. It can be seen that α_c increases as the value of C increases and goes to infinity as the value of C becomes ∞ . The reason for this is that when C increases only the droplets with q_{ij} close to unity are allowed to coalesce. This means that the number of collisions per unit time decreases and reaches zero when C approaches ∞ . Hence the value of α_c tends to infinity, to allow a finite change in the number of droplets.

A large value of C or $C \rightarrow \infty$ (which indicates that only droplets of equal radius can coalesce) is physically not reasonable because coalescence between particles of unequal radius has been observed experimentally. The value of α_c for C = 0 differs only by ± 3.0% from that calculated for C = 6. A value of C = 0 is also not possible for reasons discussed earlier in the theoretical section.

From Fig. 13 the following conclusion can be drawn regarding the effect of the constant C on α_c . For values of C ranging between 1 and 6,

Fig. 13 The effect of the value of the constant C on the coalescence efficiency coefficient. For values of C between 0 and 6, α_c changes with $\pm 2\%$. The values of α_c were calculated for $(\bar{a}, \sigma) =$ $(0.30 \ \mu m, \ 0.35)$ and $G = 10 \ s^{-1}$.





 α_{c} depends weakly on C and, therefore, the recommended value of C is between 1 and 6 where α_{c} varies by $\pm 2\%$, which is much smaller than the experimental error in α_{c} (~ 8%).

CONCLUDING REMARKS

The coalescence efficiency between emulsion droplets is an indication of their stability. In this chapter a method to investigate the orthokinetic coalescence efficiency based on comparing experimentally measured (in a microcouette apparatus) and theoretically calculated light transmittance intensities was described. Based on theoretical calculations of solid spheres of equal and different sizes, as well as studying their trajectories in simple shear flow, the orthokinetic coalescence efficiency was assumed to be a function of the droplets radius ratio. Moreover, the theory of coagulation of solid particles in shear flow showed that for particles of certain surface potential, the orthokinetic coalescence efficiency is zero when the radius of the particle exceeds a certain value. Therefore, a critical radius, a, above which the orthokinetic coalescence efficiency is equal to zero was incorporated in the function that describes the dependence of the orthokinetic coalescence efficiency on the radius ratio.

It was assumed that the orthokinetic coalescence efficiency is weakly dependent on the initial droplet radius distribution. The effect of the initial droplet radius distribution, as well as the value of the critical radius a_c and the exponent C, were discussed. From the above we can draw the following conclusions:

- 1. Estimating the orthokinetic coalescence efficiency is possible by direct comparison of experimental and theoretical values of light transmittance intensities.
- 2. For the system in question, the orthokintic coalescence efficiency found in this way is a weak function of the initial droplet radius distribution, the critical radius above which α_c is zero and the value of the exponent C between 1 and 6, which describes the form of the dependence of α_c on the radius ratio.

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NOMENCLATURE

webs -

, we say a substitution $(0,\infty) = (0,\infty) = (0,\infty) = (0,\infty)$

O

•

a	- radius, m.
	ā - mean radius.
	a_{c} - critical radius above which $\alpha_{c} = 0$.
	a _n - parameter given by Eq. [20].
	a* - dimensionless radius defined by Eq. [10].
A	- Hamaker constant, J.
A	- constant defined by Eq. [23], dimensionless.
b_	- parameter given by Eq. [21], dimensionless.
с С	- constant used in Eq. [8a], dimensionless.
d	 minimum distance between the closed and limiting trajectories,
	m.
F	- force, N.
	- F - van der Waal's attraction forces.
	- F - Brownian forces.
	- F - external forces.
	- F - gravitational forces.
	- F - net forces.
	- F - electrostatic repulsive forces.
G	- shear rate, s^{-1} .
I	- light intensity, J/m ² .
J ₁	- Bessel's function of first order.
k	- Boltzmann constant, J/ [°] K-molecule.
	k_1, k_2, k_3 and k_4 : constant used in Eq. [D-8a].
m	- refractive index ratio, dimensionless.

n*	- fraction of droplets, dimensionless.	
n	 refractive index of the continuous medium, dimensionless. 	
N	- total number of droplets at t = 0, particle/ m^3 .	
p	- pressure, N/m ² .	
d''	- droplets radii ratio, dimensionless.	
Q	 light extinction coefficient, dimensionless. 	
Q	- light scattering coefficient, dimensionless.	
r	- distance from the center of the plates at which the laser light	
	falls, m.	
R	- radius of the plates, m.	
t	- time, s.	
t*	- dimensionless time defined by Eq. [11].	
Т	- aboslute temperature, [°] K.	
v	- velocity, m/s.	
v	- volumle, m ³ .	
W	- weight fraction, dimensionless.	
W	- stability ratio, dimensionless.	
х	- parameter defined by Eq. [19].	
Y	- parameter defined by Eq. [22], dimensionless.	
Y,	- Bessel's function of first order.	
Greek		
α	- orthokinetic coalescence efficiency coefficient, dimensionless.	
α	- orthokinetic coalescence efficiency, dimensionless.	
r	- surface tension, N/m.	
Δ	 difference between experimentally measured and theoretically 	
	calculated I_t/I_o , dimensionless.	

ε	 permittivity of vacuum, Farad/m.
ξ	- function related to Hankel's functions of second order.
λ	- wavelength of light, m.
μ	- viscosity of the continuous media, Pas.
ρ	- density, kg/m ³ .
σ	- standard deviation, dimensionless.
τ	- turbidity, m ⁻¹ .
ψ	- surface potential, V.
ψ	- Ricatti-Bessel's functions.
Ω	- angular velocity, s ⁻¹ .
Script	
1	- distance between the two plates, m.

APPENDIX 3-A

A. 41

A LISTING OF THE FORTRAN SUBROUTINE COALESCE THAT INTEGRATES SHEAR INDUCED SMOLUCHOWSKI'S COALESCENCE EQUATION

SUBROUTINE COALESCE

```
C THIS SUBROUTINE CALCULATES THE EVOLUTION OF PARTICLES
C WITH THE DIMENSIONLESS TIME, T*=4*G*TN*ALPHAC*AM**3*T/3.
C WHERE
         = SHEAR RATE
         = TOTAL NUMBER OF DROPLETS PER UNIT VOLUME
CG
C TN
C ALPHAC = COLLISION EFFICIENCY COEFFICIENT
         = MEAN DISTRIBUTION RADIUS
C AM
C IT ALSO CALLS THE FOLLOWING SUBROUTINES
      1. SUBROUTINE LOGNORM TO CALCULATE THE INITIAL LOG
С
         NORMAL DROPLET RADIUS DISTRIBUTION.
С
С
      2. SUBROUTINE MISCAT TO CALCULATE THE SCATTERING
С
С
          CROSS SECTION.
С
       3. SUBROUTINE TIMEINC TO INCREASE THE TIME.
С
С
       4. SUBROUTINE RUNGKUT TO INTEGRATE SMOLUCHOWSKI
 С
          EQUATION USING RUNGA-KUTTA FOURTH ORDER METHOD.
 С
 С
 C THE PROGRAM NEEDS THE FOLLOWING DATA AS INITIAL
 C CONDITIONS
 С
            : INTEGRATION STEP
       DT
            : MEAN RADIUS OF THE DISTRIBUTION
 С
 С
       AM
       SIG : STANDARD DEVIATION
       RMAX : THE MAXIMUM RADIUS ABOVE WHICH ALPHA=0.
 С
 С
             : THE EXPONENT
       JMAX : THE NUMBER OF THE INITIAL CLASSES
 С
 С
 С
       IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION DN(6000)
       COMMON/CINT/T, DT, JS, JN, DXA(6000), XA(6000), IO, JS4, JMAX
        COMMON/SCAT/QSCA(6001), AP(6001), QZ(6001), TN
  С
 C****** INITIATION SECTION *****
  С
        DATA PI,TMAX/3.1415927,0.3/
        W=1./3.
        DO 988 IA= 1,6000
        AP(IA)=.1*((DBLE(IA)*10.0)**W)
        988 CONTINUE
        CALL LOGNORM(SIG,AM,10.0)
        CALL MISCAT(1, JMAX)
  C DROPLET ABOVE CERTAIN CLASS, ISTART, DO NOT COALESCE.
  C THIS PORTION OF THE PROGRAM CALCULATES ISTART. THIS HELPS
  C IN SAVING A LOT OF COMPUTATION TIME.
```

```
С
```

```
TAIL=0.0D0
     VOL2=0.0D0
     ISTART=2*IDINT(((10.0*RMAX)**3)/10.0)
     DO 13 I=ISTART+1, JMAX
     TAIL=TAIL+QSCA(I) *QZ(I) * (AP(I) **2)
     VOL2=VOL2+(AP(I)**3)*QZ(I)
      CONTINUE
  13
C THIS PORTION OF THE PROGRAM CALCULATES THE TOTAL NUMBER
C OF DROPLETS USING THE INITIAL VOLUME FRACTION
С
      VOL3=0.0D0
      DO 15 I=1,ISTART
   15 VOL3=VOL3+(AP(I)**3)*QZ(I)
      TN=4.77464D8/(VOL2+VOL3)
С
C***** DERIVATIVE SECTION ******
С
  102 VARAN=0.D0
C STOP THE PROGRAM WHEN THE REQUIRED TIME, TMAX IS REACHED.
С
       IF (T.GT.TMAX) GO TO 120
       V=0.0D0
       SUM=0.
       TNP=0.0D0
       CVOL=0.0D0
       TCNP=0.0D0
 С
 C CALCULATE dn/dt* FOR ALL CLASSES.
 С
       DO 104 I=1, JMAX
       WA=0.0D0
       WH=0.0D0
       IF(QZ(I) .LT. 1.0D-100 )QZ(I)=0.0D0
       TURBID=QZ(I)*QSCA(I)*(AP(I)**2)
       VARAN=VARAN+TURBID
       DO 105 J=1,JMAX
       IF (AP(J) .GE. RMAX) GO TO 106
       IF (AP(I) .GE. RMAX) GO TO 107
        RSTAR=(AP(I)/AP(J))
        IF((RSTAR .LT. 0.1) .OR. (RSTAR .GT. 10.0)) GO TO 107
        BNEW1=(4.0*RSTAR/((1.0+RSTAR)**2))**C
        BNEW=BNEW1*((1.0+RSTAR)**3)*QZ(J)*QZ(I)*(AP(J)/AM)**3
        WH=WH+BNEW
    107 KI=DABS(I-J)
        IF (AP(KI) .GE. RMAX ) GO TO 105
        IF ((KI+J) .NE. I) GO TO 105
        IF (KI .EQ. 0 ) GO TO 105
        RSTAR=(AP(KI)/AP(J))
```

```
IF((RSTAR .LE. 0.1) .OR. (RSTAR .GE. 10.)) GO TO 105
     CNEW1=(4.0*RSTAR/((1.0+RSTAR)**2))**C
     CNEW=CNEW1*((1.0+RSTAR)**3)*QZ(KI)*QZ(J)*
    +(AP(J)/AM)**3
     WA=WA+CNEW
 105 CONTINUE
 106 FNEW=WA/2.D0
      DN(I) = (FNEW-WH)
      SUM=SUM+DN(I)*(AP(I)**2)*QSCA(I)*1.0D-8
      TCNP=TCNP+DN(I)
      CVOL=CVOL+(AP(I)**3)*DN(I)*1.D-12
      V=V+(AP(I)**3)*QZ(I)
      TNP=TNP+QZ(I)*TN
      CONTINUE
 104
C CALCULATES THE TRANSMITTANCE AND THE VOLUME OF THE
С
C DROPLETS TO CHECK THAT THE MASS IS CONSERVED, AT ANY
C TIME=T.
С
      TRAN=DEXP(-PI*0.23*TN*1.0D-8*(VARAN+TAIL))
      V=4.*PI*(V+VOL2)*TN*1.D-12*50./3.
С
C****** INTEGRATION SECTION ******
С
  116 CALL TIMEINC(T, DT, 4)
      DO 118 LO=1,JMAX
       CALL RUNGKUT (QZ (LO), DN (LO))
  118 CONTINUE
С
C CONTINUE FOR ANOTHER VALUE OF T CALCULATED BY THE
C SUBROUTINE TIMEINC.
С
       GO TO 102
С
  **** FORMAT SECTION ****
С
С
   120 RETURN
       END
 С
 С
 С
       SUBROUTINE TIMEINC (TD, DTD, IOD)
       IMPLICIT REAL*8(A-H,O-Z)
       COMMON/CINT/T, DT, JS, JN, DXA(6001), XA(6001), IO, JS4, JMAX
       IO=IOD
       JN=0
       GO TO (6,5,1,1),IO
     6 JS=2
       GO TO 7
     5 JS=JS+1
       IF (JS .EQ. 3) JS=1
```

```
120
```

```
IF (JS .EQ. 2) RETURN
  7 DT=DTD
  3 TD=TD+DT
    T=TD
    RETURN
  1 JS4 = JS4 + 1
    IF (JS4 .EQ. 5)JS4=1
    IF (JS4 .EQ. 1) GO TO 2
    IF (JS4 .EQ. 3) GO TO 4
    RETURN
  2 DT=DTD/2.D0
    GO TO 3
   4 TD=TD+DT
     DT=2.D0*DT
     T=TD
     RETURN
     END
     SUBROUTINE RUNGKUT(X, DX)
     IMPLICIT REAL*8(A-H,O-Z)
     COMMON /CINT/T, DT, JS, JN, DXA(6001), XA(6001), IO, JS4
     JN=JN+1
     GO TO (9,8,3,3),IO
   9 X=X+DX*DT
     RETURN
   8 GO TO (1,2),JS
   1 DXA(JN) = DX
     X=X+DX*DT
     RETURN
   2 X=X+(DX-DXA(JN))*DT/2.D0
     RETURN
   3 GO TO (4,5,6,7), JS4
   4 XA(JN) = X
      DXA(JN) = DX
     X=X+DX*DT
      RETURN
    5 DXA(JN)=DXA(JN)+2.D0*DX
      X=XA(JN)+DX*DT
      RETURN
    6 DXA(JN)=DXA(JN)+2.D0*DX
      X=XA(JN)+DX*DT
      RETURN
    7 DXA(JN) = (DXA(JN) + DX)/6.D0
      X=XA(JN)+DXA(JN)*DT
      RETURN
      END
C **SUBROUTINE TO CALCULATE THE INITIAL SIZE DISTRIBUTION**
С
      SUBROUTINE LOGNORM (SIG, AM, BMULT)
```

C C

```
121
```

```
IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION ERF(6001)
     COMMON/SCAT/QSCA(6001), AP(6001), QZ(6001), TN
      COMMON/CMAX/JMAX
      COMMON/HASAN1/ER
      FROFPA=0.
      W=1./3.
C INTEGRATES THE PROBABILITY DISTRIBUTION FUNCTION OVER THE
C SIZE OF EVERY CLASS STARTING BY ~ 0.
С
      XSTART=1.0D-200
      X1=(DLOG(XSTART/AM)/(1.4142136D0*SIG))
С
C THE SUBROUTINE ERROR CALCULATES THE EROR FUNCTION OF THE
C ARGUMENT WHICH IS NEEDED TO CALCULATE THE FRACTION OF THE
C PARTICLES IN EVERY CLASS AS MENTIONED IN CHAPTER 2.
С
      CALL ERROR(X1)
      ERN=ER
  669 HINDEX=BMULT/2.0D0
      DO 13 IEG=1,6000
      HINDEX=HINDEX+BMULT
      RK1=0.1*(HINDEX)**W
      X1=(DLOG(RK1/AM)/(1.4142136D0*SIG))
      CALL ERROR(X1)
      ERF(IEG) = ER
       IF (IEG .NE. 1) QZ(IEG) = .5 * (ERF(IEG) - ERF(IEG-1))
       IF (IEG .EQ. 1) QZ(IEG) = .5*(ERF(IEG) - ERN)
       FROFPA=FROFPA+QZ(IEG)
    13 CONTINUE
    14 JMAX=IEG
       RETURN
       END
С
 С
 С
 C***** SUBROUTINE TO CALCULATE THE ERROR FUNCTION *****
 С
       SUBROUTINE ERROR(X)
       IMPLICIT REAL*8(A-H,O-Z)
       COMMON/HASAN1/ER
       Z1=DABS(X)
       IF (X .GT. 26.5) ER=1.
       IF (X .LT. -26.5) ER=-1.
       IF ((X .GT. 26.5).OR. (X.LT.-26.5)) RETURN
       T=1./(1.+.5*Z1)
    23 ERFCC=T*DEXP(-Z1*Z1-1.26551223+T*(1.00002368+T*
      +(.37409196+T*(.09678418+T*(-.18628806+T*
      +(.27886807+T*(-1.13520398+T*(1.48851587+T*
      +(-.82215223+T*.17087277))))))))))))
```

IF (X.LT.0.) ERFCC=2.-ERFCC ER=1.-ERFCC RETURN END

.

.

.

APPENDIX 3-B

MATHEMATICAL DERIVATION WHICH ILLUSTRATES THE ESTIMATION OF

 α_{c} at t = 0.

Differentiation of Eq. [17] with respect to t gives

$$d(I_{t}/I_{o})dt = -(I_{t}/I_{o})\pi IN_{o}d/dt (\sum_{i}^{\infty} n_{i}^{*}Q_{s}, a_{i}^{2})_{i}.$$
 [B-1]

The derivative of the summation on the right side of Eq. [B-1] can be written as

$$\frac{d}{dt} = (\sum n_i^* Q_i a_i^2) = \sum_i^{\infty} \frac{d}{dt} (n_i^* Q_{s,i} a_i^2) = \sum_i^{\infty} n_i^* d(Q_i a_i^2) / dt + Q_{s,i} a_i^2 dn_i^* / dt) ,$$
[B-2]

but $d/dt(Q_{s,i}n_i^*) = 0$, since the initial distribution and the droplets that might appear due to the coalescence process are divided into classes each of fixed a_i ; hence a_i and Q_i are not functions of time. Moreover,

$$t^* = \frac{16}{3} GN_o \bar{a}^3 \alpha_c t$$
, [B-3]

hence, combining Eqs. [B-1,2,3] gives

$$\frac{d(I_t/I_o)}{dt} = -\frac{16}{3} N_o^2 \bar{a}^3 G \pi \alpha_c I(I_t/I_o) \sum_{i}^{\infty} (Q_{s,i} a_i^2 dn_i^*/dt^*)$$
[B-4]

To estimate α_c , the above variables should be calculated at t = 0.

APPENDIX 3-C

PHOTOGRAPH OF MICROCOUETTE APPARATUS USED TO INDUCE SHEAR COALESCENCE THE LASER LIGHT SOURCE, SPEED MOTOR, GLASS PLATES, PHOTODIODE, DATA ACQUISITION SYSTEM AND COMPUTER CAN BE SEEN



APPENDIX 3-D

SOLUTION OF THE CONTINUITY EQUATION AND THE NAVIER-STOKES EQUATION FOR FLOW IN THE MICROCOUETTE APPARATUS

For a cylindrical coordinate system, the r, $\boldsymbol{\theta}$ and z components of the equation of motion are:

r-component:

$$\frac{-\rho v_{\theta}^2}{r} = \frac{\partial p}{\partial r} . \qquad [D-1a]$$

0-component:

$$\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r v_{\theta}) \right) + \frac{\partial^2 v_{\theta}}{\partial z^2} = 0 . \qquad [D-1b]$$

z-component:

$$\frac{\partial p}{\partial z} + \rho g_z = 0 . \qquad [D-1c]$$

where v_{θ} is the velocity in the θ direction, p is the pressure and g_z is the constant of gravity.

In the creeping flow regime where $\text{Re} = pv_{\theta}l/\mu \ll 1.0$, the r-component of the equation of motion reduces to $\partial p/\partial r = 0$ or p is only a function of z. In fact, $p = -\rho gz$ as the z-component of the equation of motion indicates. Then we are lift with the θ -component to solve. We postulate that the velocity distribution will be of the form

 $\mathbf{v}_{\boldsymbol{\theta}} = f(\mathbf{r})g(\mathbf{z}) \quad [D-2]$

Upon substitution of Eq. [D-2] in Eq. [D-1b], we obtain

$$\frac{1}{f}\frac{d^2f}{dr^2} + \frac{1}{rf}\frac{df}{dr} - \frac{1}{r^2} = -\frac{1}{g}\frac{dg^2}{dz^2}$$
[D-3]

We can let both sides of Eq. [D-3] be equal to λ^2 . Therefore we can write

$$\frac{1}{f}\frac{d^{2}f}{dr^{2}} + \frac{1}{rf}\frac{df}{dr} - \frac{1}{r^{2}} = \lambda^{2}$$
[D-4]

and

.

$$\frac{1}{g}\frac{d^2g}{dz^2} = -\lambda^2 . \qquad [D-5]$$

The solution of Eqs. [D-4] and [D-5] for any value of $\lambda > 0$, respectively, is

$$f(r) = C_1 I_1(\lambda r) + C_2 K_1(\lambda r)$$
 [D-6]

$$g(z) = C_{3}\cos(\lambda z) + C_{4}\sin(\lambda z) , \qquad [D-7]$$

where I_1 and K_1 are modified Bessel's functions of order 1. The velocity $v_{\theta} = f(r)g(z)$ then takes the following form:

$$v_{\theta} = k_1 I_1 (\lambda r) \cos(\lambda z) + k_2 K_1 (\lambda r) \cos(\lambda z) + k_3 I_1 (\lambda r) \sin(\lambda z) + k_4 K_1 (\lambda r) \sin(\lambda z) , \qquad [D-8a]$$

where k_1 , k_2 , k_3 and k_4 are equal to C_1C_2 , C_2C_1 , C_4C_1 and C_4C_2 , respectively. Since this solution is valid for any value of $\lambda > 0$, we can rewrite Eq. [D-8] as

$$v_{\theta} = \lim_{\epsilon \to 0} \int_{\epsilon}^{\infty} [k_{1}I_{1}(\lambda r)\cos(\lambda z) + k_{2}K_{1}(\lambda r)\cos(\lambda z) + k_{3}I_{1}(\lambda r\sin(\lambda z) + k_{4}K_{1}(\lambda r)\sin(\lambda z)] d\lambda .$$
 [D-8b]

For the case where $\lambda = 0$ the solution of Eqs. [D-4] and [D-5], respectively, yields

$$f(r) = C_{r} + C_{r}/r$$
, [D-9]

$$g(z) = C_{7}z + C_{8}$$
, [D-10]

and the resultant solution for the case $\lambda = 0$ is

$$v_{\theta} = k_{5}rz + k_{6}r + k_{7}z/r + k_{8}/r \quad .$$
 [D-11]

Hence the general solution becomes,

$$v_{\theta} = \lim_{\varepsilon \to 0} \int_{\varepsilon}^{\infty} [k_{1}I_{1}(\lambda r)\cos(\lambda z) + k_{2}K_{1}(\lambda r)\cos(\lambda z) + k_{3}I_{1}(\lambda r)\sin(\lambda z) + k_{4}K_{1}(\lambda r)\sin(\lambda z)] d\lambda + k_{5}rz + k_{6}r + k_{7}z/r + k_{8}/r .$$
[B-12]

The following boundary conditions can be applied to determine the constants in Eq. [D-7] for the case where $l \ll R$,

at
$$r = 0$$
, $v_0 = 0$ for all value of $0 \le z \le 1$, [D-13a]

at
$$z = l$$
, $v_{\rho} = 0$ for all values of $0 \le r \le R$, [D-13b]

at
$$r = R$$
, $v_{\theta} = \Omega R$ for all $0 \le z < 1$, [D-13c]

at
$$z = 0$$
, $v_{\rho} = \Omega r$ for $0 \le r \le R$. [D-13d]

We shall consider the following cases. First we shall assume no singularity so that the terms containing 1/r are all zero and, second, the case where $\lambda = 0$, hence we are left with

$$\mathbf{v}_{\boldsymbol{\theta}} = \mathbf{k}_{5}\mathbf{r}\mathbf{z} + \mathbf{k}_{6}\mathbf{r} , \qquad [B-14]$$

with Eqs. [D-13b] and D-13d] as boundary conditions. Upon applying these boundary conditions, $v_{\mbox{$\theta$}}$ becomes

$$\mathbf{v}_{\boldsymbol{\theta}} = \Omega \mathbf{r} \left(1 - \mathbf{z}/l \right) \,. \tag{D-15}$$

In fact this is the solution which one would get by letting $v_{\theta} = rg(z)$. The shear rate $G = -\frac{\partial v_{\theta}}{\partial z}$ is

$$G = \Omega r / l.$$
 [D-16]

C

CHAPTER 4

STABILITY OF WATER IN OIL EMULSIONS IN SIMPLE SHEAR FLOW.

II. THE EFFECTS OF ADDITIVES ON THE ORTHOKINETIC COALESCENCE EFFICIENCY

ABSTRACT

The effect of electrolytes, solid particles, interfacial tension and the effect of shear rate on the orthokinetic coalescence efficiency of aqueous emulsion droplets suspended in oil was investigated. It was found that, for a given shear rate, lowering the interfacial tension lowers the coalescence efficiency. The effect of electrolytes is mainly to lower the interfacial tension of the water/oil interface, electrostatic forces play a minor role. AlCl₃ is more effective in lowering the interfacial tension than KCl, resulting in more stable emulsions in the presence of AlCl₃. This trend is opposite to that in oil/water emulsions.

The emulsions were found to be most stable at intermediate shear rates. At low and high shear rates the emulsions stability is minimum. The dependence of the coalescence efficiency on the shear rate is determined by the ratio of the attractive (van der Waals) and the repulsive forces to the hydrodynamic forces, mainly arising from drop deformation.

Similar to oil/water emulsions, the presence of solid particles at the water/oil interface plays an important role in the stability of the emulsions. It was found that the emulsions are more stable in the presence of colloidal gold particles.

INTRODUCTION

In Chapter 3 we outlined a method to determine the orthokinetic coalescence efficiency of water/silicone oil emulsions subjected to a simple shear flow. In this chapter we extend the previous work to study the effects of the presence of electrolytes, solid particles, surface active agents on the orthokinetic coalescence efficiency. Furthermore, the effects of shear rate and the interfacial tension between the water and the oil phases on the orthokinetic coalescence efficiency will be examined.

In most commerical emulsions the phases of the emulsions usually are not pure. They may contain additives so that the emulsions can be utilized for many purposes and for a long time. Therefore it is essential to study the stability of emulsions in the presence of additives.

EXPERIMENTAL DETAILS

1. Experimental Apparatus

Details of the experimental apparatus used were described in Chapter 3. For the sake of completeness, we summarize here the experimental setup briefly. It consists of a system of two parallel plates made out of a special optical glass. The upper plate cannot rotate, but it can move up or down to achieve the required gap width between the two plates. The lower plate, on the other hand, cannot move up or down but it can rotate at an adjustable angular velocity. A laser light beam (He-Ne, $\lambda = 0.633 \ \mu m$) is allowed to pass through the emulsion contained between the plates. The transmitted light intensity as a function of time is detected via a photo-

diode whose output can be seen on the display of a power meter. The signal from the power meter is sent to a data acquisition system, the output of which is received by a personal computer for further handling of the data (see Fig. 4, Chapter 3).

2. Preparation of the Emulsion

The procedures for preparing the emulsion were discussed in Chapter 3. In the case where the emulsions contain additives, the emulsion preparation was done by dissolving the additive in the water phase first and the rest of the procedures are as discussed in Chapter 3.

The following additives were used in this study: KCl of concentrations 13.4×10^{-3} , 0.67, 1.34 M, AlCl₃ of 7.5 mM, sodium dodecyl sulfate (SDS) of 3.5 mM. The concentration of SDS was chosen such that it is below the CMC (8 mM) to avoid micelle formation (1). Also, spherical gold sols particles whose mean radius is 5 nm and concentration of 0.05 g gold per liter were used. The gold sols studied were the same as the ones studied by Schumacher and van de Ven (2) and prepared according to the procedures discussed in (3). The effect of the interfacial tension on the orthokinetic coalescence efficiency was also studied. For this purpose olive oil having the same viscosity as the silicone oil (90 mPas) but a different interfacial tension was used. The interfacial tension between the oil and the water was measured by the pendent drop method (4). The effect of shear rate on the orthokinetic coalescence efficiency was investigated by shearing the emulsion at shear rates ranging from 0 to 250 s⁻¹. Table 1 lists the physical properties of each system studied.

TABLE 1:LIST OF THE REFRACTIVE INDEX RATIO OF THE DROPLETS
TO THAT OF THE CONTINUOUS MEDIUM, m, AND THE INTER-
FACIAL TENSION BETWEEN THE TWO PHASES OF THE EMUL-
SIONS MEASURED AT 23 C.

	REFRACTIVE	INTERFACIAL
	INDEX	TENSION mN/m
MATERIAL	RATIO	
1. SILICONE OIL (97 mPas)		
DISTILLED DEIONIZED WATER	0.9515	28.2
13.4 mH KCl	0.9515	13.9
7.5 mH AlCl 3	0.9515	10.2
3.5 mM SDS	0.9515	15.4
0.67 H KC1	0.9550	17.4
1.34 M KC1	0.9596	11.8
50 g gold/L	0.28-2.221	-
2. OLIVE OIL (90 mPas)		
DISTILLED DIONIZED WATER	0.9093	13.2

RESULTS AND DISCUSSION

Some typical experimental results of $(I_t/I_o)_{exp}$ for a water/silicone oil emulsion sheared at 18 s⁻¹, a water/silicone oil emulsion where the water phase contains 1.34 mM KCl sheared at 10 s⁻¹, and for a water/olive oil emulsion sheared at 10 s⁻¹ are shown in Figs. 1-3, respectively. The analysis of the experimental data was performed as described in Chapter 3. At time = 0, every system has an initial experimental value of $(I_t/I_o)_{exp}$ which depends on the value of the refractive index ratio, m, of the droplets to that of the continuous medium and the initial droplet radius distribution. All other parameters such as the wavelength of the

Fig. 1 The change in experimentally measured light transmittance intensity, $(I_t/I_o)_{exp}$, versus time for water/silicone oil emulsions sheared at G = 18 s⁻¹. The viscosity of the silicone oil is 97 mPas.


Time, s

Fig. 2 The change in the experimentally measured light transmittance intensity, $(I_t/I_o)_{exp}$, versus time for water/silicone oil emulsion sheared at G = 10 s⁻¹. The water phase contains 1.34 M KCl. The viscosity of the silicone oil is 97 mPas.



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Fig. 3 The change in the experimentally measured light transmittance intensity, $(I_t/I_o)_{exp}$, versus time for water/olive oil emulsion sheared at 10 s⁻¹. The oscillations appearing in the figure are due to imperfect adjustment of the plates.

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light, the concentration of the dispersed phase, etc., are kept constant. Because the orthokinetic coalescence efficiency is a weak function of the initial droplet radius distribution (see Chapter 3), different log normal distributions of a wide range of mean radius, \overline{a} , and standard deviation, σ , which give a transmitted light intensity $(I_t/I_o)_{cal}$, such that

$$(I_{\downarrow}/I_{o})_{exp} - E_{i} \leq (I_{\downarrow}/I_{o})_{cal} \leq (I_{\downarrow}/I_{o})_{exp} + E_{2}$$

were searched, E_1 and E_2 are arbitrary numbers that were chosen such that the values of (I_t/I_o) lie within the range given by the above equation. For example, if $(I_t/I_o)_{exp}$ is 0.25 then all log normal distributions which give $(I_t/I_o)_{cal}$ between 0.2 and 0.3 were searched. In this case E_1 and E_2 These log normal distributions form approximately a triare 0.05 each. angle whose corners are named a, b and c, as can be seen in Fig. 10 of Chapter 3. All the calculations were done for the log normal distribution designated by point d, which is the closest one to the actual distribution based on turbidimetric and optical microscopy analysis, as discussed in Chapter 2. Although the real droplet size distribution is closer to a bimodal than a log normal one, we showed that the coalescence efficiency obtained does not depend strongly on the precise choice of the For computational convenience we approximate here the distribution. distribution by a log normal one. Values of $(I_t/I_o)_{exp}$ at t = 0 for every system studied, $(I_t/I_o)_{exp} - E_1$, $(I_t/I_o)_{exp} + E_1$, the points a, b, c and d are listed in Table 2.

		+ E ₂ ,	a, b, c and d.					
SYSTEM	G, =	(I / I) $(t \circ exp)$	$(I \downarrow I) = E_1$	(I_/I_) +E t_oexp 2	a (a μm,σ)	b (āμm,σ)	с (ā μ n ,σ)	d (a μa,σ)
phase)		(t = 0)						
THE CONTINUOUS IS SILICONE OIL (97 mPas) DISTILLED DE- IONIZED WATER """ """ """	0 10 136 199 245	0. 232 0. 244 0. 314 0. 218 0. 273	0.2 0.2 0.2 0.2 0.2	0.4 0.4 0.4 0.4 0.4	(0.34, 0.01) (0.34, 0.01) (0.34, 0.01) (0.34, 0.01) (0.34, 0.01) (0.34, 0.01)	(0.57,0.01) (0.57,0.01) (0.57,0.01) (0.57,0.01) (0.57,0.01) (0.57,0.01)	(0.11,0.7) (0.11,0.7) (0.11,0.7) (0.11,0.7) (0.11,0.7) (0.11,0.7)	(0.3, 0.35) (0.3, 0.35) (0.3, 0.35) (0.3, 0.35) (0.3, 0.35) (0.3, 0.35)
WATER CONTAIN- ING 13.4 mM KCl	10 135 238	0.288 0.332 0.238	0.2 0.2 0.2	0.4	(0.34, 0.01) (0.34, 0.01)	(0.57,0.01) (0.57,0.01)	(0.11,0.7) (0.11,0.7)	(0.3, 0.35) (0.3, 0.35)
WATER CONTAIN- ING 7.5 mM A ^{1C1} 3	127 135 195 241	0.325 0.281 0.355 0.275	0.2 0.2 0.2 0.2	0.4 0.4 0.4 0.4	(0.34,0.01) (0.34,0.01) (0.34,0.01) (0.34,0.01)	(0.57,0.01) (0.57,0.01) (0.57,0.01) (0.57,0.01)	(0.11,0.7) (0.11,0.7) (0.11,0.7) (0.11,0.7)	(0.3, 0.35) (0.3, 0.35) (0.3, 0.35) (0.3, 0.35)
WATER CONTAIN- ING 3.5 mM SDS	0 1.0	0.133 0.1	0.09 0.09	0.1 0.1	(0.68,0.01) (0.68,0.01)	(0.88,0.01) (0.88,0.01)	- - (0.02.0.87	(0.5, 0.38) (0.16, 0.35
WATER CONTAIN- ING 0.67 M KC1	10	0.548	0.5	0.6	(0.24,0.01)	(0.28, 0.01)	(0.02,0.87) (0.1, 0.35
WATER CONTAIN- ING 1.34 H KC1	0 10	0.690 0.723	0.6	0.75	(0.22,0.1)	(0.28, 0.01)	(0.01, 1.0)	(0.2, 0.36
WATER CONTAIN- ING 50 g gold/L	. 10	0.333	0.3	0.4	(0.28,0.01)			
THE CONTINUOUS PHASE IS OLIVE				0.4	(0.14.0.01)	(0.16,0.01) (0.1,0.09)	(0.1, 0.3)
DISTILLED DE-	0	0.355 0.352	0.3	0.4	(0.14, 0.01)	(0.16,0.01) (0.1,0.09)) (0.1,0.3

TABLE 2: A LIST OF THE VALUES OF (I / I) for the systems shown in to exp COLUMN 1, THE APPLIED SHEAR RATE, $(I_{t}/I_{o}) = E_{t}$, $(I_{t}/I_{o}) = E_{t}$ ν L_{pol}t

IONIZED WATER

Values of $(I_t/I_o)_{cal}$ were calculated from (5)

$$\frac{I_{t}}{I_{o}} = \exp\left[-\left(\pi l N_{o} \sum_{i=1}^{\infty} n_{i}^{*} Q_{g,i} a_{i}^{2}\right)\right], \qquad [1]$$

where N_o is the total number of droplets per unit volume at t = 0, *l* is the gap width the light beam travels through the emulsion, n_i^* is the fraction of droplets in class i whose radius is a_i , and $Q_{s,i}$ is the scattering cross section efficiency of the droplets of class i. $Q_{s,i}$ is a function of the refractive index ratio of the droplets to that of the continuous media, the wavelength of the light beam and the radius of the droplets.

The values of n_i^* at t = 0 for a given log normal distribution characterized by \overline{a} and σ which can be expressed as

$$P(\overline{a},\sigma) = \exp\{-\left[\ln(a/\overline{a})\right]^2/(2\sigma^2)\}/(\sigma\overline{a}\sqrt{2\pi}), \qquad [2]$$

were calculated from

$$n_{i}^{*} = \int_{a_{i}}^{a_{i+1}} P(\overline{a},\sigma) da = 0.5 [erf(Z_{i+1}) - erf(Z_{i})], \qquad [3]$$

where

$$Z_{i} = \frac{\ln(a_{i}/\bar{a})}{\sigma\sqrt{2\pi}} .$$
[4]

Once n_i^* at t = 0 is calculated, then the change of n_i^* with time can be followed by solving Smoluchowski's equation written in dimensionless form as

$$\frac{dn_{i}^{*}}{dt^{*}} = \frac{1}{2} \sum_{j+k=i} \sum_{k=i} n_{k}^{*} n_{j}^{*} (a_{j} / \overline{a}) (1 + q_{ij})^{3} (\alpha_{o} / \alpha_{c}) - n_{i}^{*} \sum_{j=1} n_{i}^{*} (a_{j} / \overline{a}) (1 + q_{ij})^{3} (\alpha_{o} / \alpha_{c})$$
[5]

where

$$t^* = \frac{4}{3} N_{o} Ga^{-3} \alpha_{c} t , \qquad [6]$$

$$\mathbf{n}_{i}^{*} = \mathbf{n}_{i} / \mathbf{N}_{o}$$
[7]

$$q_{ij} = a_i / a_j , \qquad [8]$$

and α_{o}/α_{c} is given by the following function

,

$$\alpha_{o} / \alpha_{c} = \begin{cases} \left[\frac{4q_{ij}}{(1 + q_{ij})^{2}} \right]^{C}, & a < a_{c} \\ 0, & a > a_{c} \end{cases}$$
[9]

In the above equation α_c is the coalescence efficiency coefficient, a_c is the maximum size above which coalescence between droplets does not occur, and C is an adjustable parameter. The significance of a_c and C and their effect on α_c was discussed in Chapter 3 where it was found that α_c is a weak function of a_c and C ranges between 1 and 6.

The coalescence efficiency coefficient, α_c is a function of the interfacial tension between the water phase and the oil phase, γ , the surface potential of the droplets, ψ , the Hamaker constant of the system, A, the viscosity and the density of the continuous medium, μ_o and ρ_o , respectively, the dielectric constant of the continuous medium, ε , and the applied shear rate.

1. Effect of the Shear Rate on α_{c}

The orthokinetic coalescence efficiency was calculated for point d of Fig. 10 in Chapter 3 which corresponds to $(\overline{a},\sigma) = (0.3 \ \mu m, 0.35)$. The estimated values of α_c versus the dimensionless number Gt for water/silicone oil emulsion are shown in Fig. 4. It can be seen that α_{c} depends on the value of G. To illustrate the dependence of α_{c} on G, α_{c} is plotted against G at $t^* = 0$. The results are depicted in Fig. 5. Early work of van de Ven and Mason (6) showed a similar dependence of α_c on G (cf. Fig. 3 of Chapter 1). They investigated the collision efficiency as a function of shear rate for two hard spheres of equal radius in the presence of both van der Waals attractive forces and electrical repulsive forces. They found that the collision efficiency decreases as the shear rate increases until a critical shear rate is reached. Beyond this critical shear rate the collision efficiency decreases as G increases. This relationship continues until a second critical shear rate is reached where the collision efficiency increases as the shear rate increases.

The reason for the behavior shown in Fig. 5 can be explained as follows. In the presence of shear, hydrodynamic forces, shear forces and

Fig. 4 The coalescence efficiency coefficient versus Gt for water/ silicone oil emulsion subjected to various shear rates calculated for C = 1.0 and $a_c = 2.0 \ \mu m$. The viscosity of the silicone oil is 97 mPas.



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Fig. 5 The coalescence efficiency coefficient versus G for water/silicone oil emulsion at t* = 0. Calculated for C = 1.0 and $a_c = 2.0 \mu m$. The viscosity of the silicone oil is 97 mPas.



deformation of droplets become important. The shear forces and the hydrody namic resistance are expressed by the following equations (7)

$$F_{\text{phear}} = G\mu \overline{a} \, \hat{g}(r,q) \sin^2 \theta \sin 2\phi , \qquad [10]$$

$$F_{hyd} = \frac{3\pi\mu\bar{a}u}{C(r,q)} , \qquad [11]$$

where $\overline{a} = (a_1 + a_2)/2$, a_1 and a_2 being the radii of the colliding droplets, g(r,q) is a known function of the separation r and q, C(r,q) is a correction factor for Stokes law taking into account the presence of the second droplet, and u is the relative droplet velocity. The shear forces tend to increase the coalescence efficiency between the emulsion droplets. The hydrodynamic resistance and the deformation of the droplets, on the other hand, tend to decrease the coalescence efficiency. At any shear rate, if the shear forces and van der Waals attraction forces dominate the hydrodynamic resistance, the deformation effect and the repulsive forces, then an increase in the coalescence efficiency results or vice versa.

As the shear rate increases, the hydrodynamic resistance between the droplets increases too. As a result of this the chance for the droplets to coalesce decreases and so α_c decreases. In addition to this, the deformation of the droplets (even if it is very small) due to the shearing action becomes very important. Thus the time it takes for two droplets to coalesce becomes longer, which reflects in a lower collision efficiency. However as the shear rate exceeds a certain value, the shear forces are large enough that the droplets can jump over the energy barrier and coalesce.

Fig. 5 indicates that at a low shear rate (G < 100 s⁻¹) the attraction forces between droplets overcome the repulsive and hydrodynamic resistance forces and hence α_c is high. At a high shear rate (G > 200 s⁻¹), the repulsive forces become negligible compared to that of the shear forces. Also, the shear forces dominate the hydrodynamic resistance and the deformation effect and, therefore, the value of α_c is high. Increasing the shear rate further will cause more deformation and, therefore, α_c will decrease to zero, similar to the hard sphere case but more rapidly. On the other hand, at a moderate shear rate (100 < G < 200 s⁻¹), the hydrodynamic resistance, the electrostatic repulsive forces and the deformation effects are stronger than van der Waals attraction forces and the shear forces, and so the coalescence efficiency is low. The shear rate is related to the capillary number Ca = ($\overline{a}G\mu/\gamma$) and a figure relating the qualitative dependence of α_o on C_A where Ca is a parameter similar to that shown in Fig. 2, Chapter 1, where C_b is a parameter is depicted in Fig. 6.

The effect of G on α_c was also studied in the presence of 13.4 mM KCl, 7.5 mM AlCl₃ and 3.5 mM SDS. The emulsions where KCl and AlCl₃ are present in the water phase have the same range of $(I_t/I_o)_{exp}$ as that of the pure water case (note that the presence of the additives does not change the refractive index of the water, see Table 1). Therefore the calculations of α_c were done for the same initial droplet size distribution $(\bar{a}, \sigma) = 0.3 \ \mu m$, 0.35). In the case of SDS, the initial transmittance light intensity ranged between 0.09 and 0.15. Therefore all possible log normal droplet radius distributions which give $(I_t/I_o)_{cal}$ between 0.09 and 0.15 were searched. These distributions form a triangle similar to the one shown in Fig. 10, Chapter 3. The corners of this triangle, represented by a, b, and c, are

Fig. 6 The dependence of α_0 on the dimensionless C_A number where the dimensionless number Ca is a parameter is qualitatively shown.



 $\text{Log}(C_A^{-1})$

shown in Table 2. The calculations of α_c were done for point d at the center of the triangle which corresponds to $(\bar{a}, \sigma) = (0.5 \ \mu m, 0.38)$ (see Table 2). Calculated values of α_c versus Gt for KCl, AlCl₃ and SDS are presented in Figs. 7, 8 and 9, respectively. The dependence of α_c on G at $t^* = 0$ for these cases is shown in Figs. 10, 11 and 12. From these plots one can see the effects of shear on α_c , as discussed earlier. The effects of electrolytes on α_c will be discussed in the next section.

2. Effect of the Presence of KCl, AlCl₃ and SDS on α_c

The effects of KCl, AlCl₃ and SDS on the orthokinetic coalescence efficiency coefficient can be seen from Figs. 10-12. It can be noticed that at low and high shear rates these additives stabilize the emulsions since α_{c} is lower. At a moderate shear rate the effect is just the opposite, they seem to destabilize the emulsions. A possible reason for this is as follows. Besides changing the initial droplet radius distribution, the presence of these additives also changes the surface potential of the droplets as well as the interfacial tension (Table 1). The change of the surface potential changes the ratio of the repulsive forces to the attraction forces. Note that since the additives are dissolved in the water phase, the main changes possibly take place in the water phase and the possible changes that might take place in the continuous phase (oil phase) are not known. However these additives decrease the interfacial tension between the water and the oil phases. Hence the droplets become more deformable and α_c , in the case of additives, is smaller than that of the pure water case. The change in the ratio of the attractive forces to that of

Fig. 7 The collision efficiency coefficient versus Gt for water/silicone oil emulsion subjected to various shear rates calculated for C = 1.0 and $a_c = 2.0 \ \mu\text{m}$. The water phase contains 13.4 mM KCl. The viscosity of the silicone oil is 97 mPas.



Fig. 8 The collision efficiency coefficient versus Gt for water/silicone oil emulsion subjected to various shear rates calculated for C = $1.0 \text{ and } a_c = 2.0 \ \mu\text{m}$. The water phase contains 7.5 mM AlCl₃. The viscosity of the silicone oil is 97 mPas. Collision Efficiency Coefficient, $\alpha_{
m C}$



Gt

Fig. 9 The coalescence efficiency coefficient versus Gt for water/silicone oil emulsion subjected to various shear rates calculated for C = 1.0 and $a_c = 2.0 \ \mu m$. The water phase contains 3.5 mM SDS. The viscosity of the silicone oil is 97 mPas.



Fig. 10 The coalescence efficiency coefficient versus G for water/silicone oil emulsion at t* = 0 calculated for C = 1.0 and $a_c = 2.0$ μ m. The water phase contains 13.4 mM KCl. The viscosity of the silicone oil is 97 mPas.

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Fig. 11 The coalescence efficiency coefficient versus G for water/silicone oil emulsion at $t^* = 0$ calculated for C = 1.0 and $a_c = 2.0$ μ m. The water phase contains 7.5 mM AlCl₃. The viscosity of the silicone oil is 97 mPas.



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Fig. 12 The coalescence efficiency coefficient versus G for water/silicone oil emulsion at t* = 0 calculated for C = 1.0 and $a_c = 2.0$ μ m. The water phase contains 3.5 mM SDS. The viscosity of the sili cone oil is 97 mPas.



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the repulsive forces also results in a different critical shear rate at which α starts to increase as G increases.

It is of interest to note that the stability of a water/oil emulsion is larger when AlCl₃ is used as an electrolyte as compared to KCl. This is contrary to aqueous dispersions for which the opposite is true. The reason is that for water/oil emulsions the electrolyte is inside the emulsion droplet, not around them in diffuse ionic double layers.

Another interesting observation that can be noticed in Fig. 12 is the dependence of α_c on G for the SDS case. The coalescence efficiency coefficient remains zero until a critical value of G is reached, beyond which it starts to increase. Such critical shear rates beyond which orthokinetic coagulation occurs are also found in other systems (8).

3. Effect of the Concentration of KCl on α_c

The orthokinetic coalescence efficiency coefficient was calculated from experimental transmittance data for the case where the concentration of KCl is 13.4×10^{-3} M, 0.67 M and 1.34 M. The calculations were done for $(\bar{a}, \sigma) = (0.3 \ \mu\text{m}, 0.35)$, $(0.16 \ \mu\text{m}, 0.35)$ and $(0.1 \ \mu\text{m}, 0.35)$ for [KCl] = 13.4×10^{-3} M, 0.67 M and 1.34 M, respectively. (Notice that the average size of the emulsion droplets formed by ultrasonification decreases with increasing salt concentration.) The results, α_c versus time, for these three concentrations are compared to the case [KCl] = 0 and are shown in Fig. 13. As can be seen from this figure, the presence of KCl has a substantial effect on α_c . The values of α_c decrease in the presence of KCl. The main reason is probably that the presence of KCl decreases the interfacial tension between the water and the oil phases (cf. Table 1). Hence the

Fig. 13 The effect of the concentration of KCl on the coalescence efficiency coefficient as a function of Gt for water/silicone oil emulsion sheared at G = 10 s⁻¹. The calculations were done for C = 1.0 and $a_c = 2.0 \ \mu m$. The viscosity of the silicone oil is 97 mPas.



droplets become more deformable which makes the time it takes for two droplets to coalesce longer, resulting in smaller values of α_c . The reason is probably that, although increasing the concentration of KCl alters the nature of the electrical double layer, this change takes place only inside the droplets and no changes occur outside the droplets because the oil is a non-conductive medium. Since the effect of the concentration on the interfacial tension is minor, only a weak dependence of α_c on the concentration of KCl was found (for [KCl] > 13 mM). The effect of the concentration of KCl on α_c can also be seen by plotting α_c versus the concentration of KCl at t* = 0, as shown in Fig. 14. For comparison, the values of γ (the interfacial tension between oil and water plus KCl) are shown as well. It can be seen that there is a strong correlation between α_c and γ , suggesting that changes in γ are the main cause for changes in α_c . Electrostatic forces appear to have only a minor effect.

4. Effect of the Interfacial Tension on α_{c}

To test the effect of the interfacial tension on α_c two systems were chosen. The first one was a water/silicone oil emulsion and the second a water/olive oil emulsion. The silicone oil and the olive oil both have very similar viscosities, ~ 90 mPas, but different interfacial tensions. The interfacial tensions of water/silicone oil and water/olive oil are 28 and 13 mN/m, respectively. The optical and the physical properties for these systems are listed in Table 1.

Values of α_c versus time were calculated from the experimental data and the results are shown in Fig. 15. It can be seen from this figure that the values of α_c for the water/olive oil emulsion are much smaller than

Fig. 14 The experimentally obtained coalescence efficiency coefficient at $t^* = 0$ versus the concentration of KCl for water/silicone oil emulsions sheared at G = 10 s⁻¹. The calculations were done for C = 1.0 and $a_c = 2.0 \ \mu m$. For comparison, interfacial tensions are shown as well.


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Fig. 15 The coalescence efficiency coefficient versus Gt for water/ silicone oil and water/olive oil emulsions sheared at 10 s⁻¹. The calculations were done for C = 1.0 and $a_c = 2.0 \ \mu m$.



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those of the water/silicone oil emulsion. The reason can be explained as follows. The coalescence process between two drops can be divided into three stages (9-10). The first step is bringing two droplets together, due to the shearing action, to a distance where the colloidal forces are important. The second step is thinning the film between the droplets. The interfacial tension plays an important role in thinning the film. When the interfacial tension is small, the rate at which the film thins is slow. When the droplets are forced against each other, forcing out the liquid in the gap between the droplets, the surfaces of the droplets deform to counteract this force. The degree of deformation is a function of the interfacial tension. When the interfacial tension is small, the droplet deforms more and, hence, the rate at which the liquid in the gap is forced out is The third step of the coalescence episode is the rupture of the slower. film which leads to coalescence of the two droplets. The coalescence time is the time it takes for these three stages to take place. The longer the coalescence time the more stable is the emulsion. Experimental results of Dickenson et al. (10) on the coalescence stability of emulsion-sized droplets at a planar oil/water interface confirm these findings. Our data on water/oil emulsions containing KCl also show the same trend.

5. Effect of the Presence of Solid Particles on α_{c}

Similar to oil/water emulsions, solid particles also stabilize water/ oil emulsions. Gold particles with a radius of 5 nm, much smaller than the radius of the water droplets (200 nm), were chosen to study the effects of solid particles on coalescence. The number of gold particles per ml water is 5.86 x 10^{14} particles. In a 0.2 μ m water droplet the number of gold

particles is ~ 19 particles. Assuming that all the gold particles migrate to the water/oil interface then the gold particles cover ~ 1% of the droplet surface. The optical properties of gold are listed in Table 1. The total light extinction from the system, $I_{s,total}$, is due to the scattering of light by the emulsion droplets $I_{s,droplets}$ and due to the scattering and the absorption of light by the gold particles, $(I_{s,} + I_{abs})_{gold}$;

$$I_{s,total} = I_{s,droplets} + (I_{s} + I_{abs})_{gold} .$$
 [12]

Therefore Eq. [1] for this case is rewritten as

$$\frac{I_{t}}{I_{o}} = \exp\{-\pi I[(N_{t}\Sigma n_{i}^{*}Q_{s,i}a_{i}^{2})_{water} + (N_{t}Q_{ext}\overline{a}^{2})_{gold}]\}, \qquad [13]$$

where Q_{ext} is the light extinction coefficient of the gold particles. In general the extinction coefficient of any material whose refractive index can be written as $n^* = n - ik$ is given by the following equation (11)

$$Q_{oxt} = \frac{24nk}{F_1} X + \left\{ \frac{4}{15} nk + \frac{20}{3F_2} nk + 4.8 nk \left[\frac{F_3}{F_1^2} \right] \right\} X^3 + \frac{8F_4}{3F_1^2} X^4 , \quad [14]$$

$$X = 2\pi a/\lambda$$

$$F_{1} = (n^{2} + k^{2})^{2} + 4(n^{2} - k^{2}) + 4$$

$$F_{2} = 4(n^{2} + k^{2})^{2} + 12(n^{2} - k^{2}) - 9$$

$$F_{3} = 7(n^{2} + k^{2})^{2} + 4(n^{2} - k^{2} - 5)$$

$$F_{4} = [(n^{2} + k^{2})^{2} + (n^{2} - k^{2} - 2)]^{2} - 36n^{2}k^{2}.$$

In the above equations n and k are the real and the imaginary part of the refractive index, λ is the wavelength of the light beam and i is the imaginary number = $\sqrt{-1}$.

For gold particles in water and at $\lambda_{air} = 0.6 \ \mu m$ the values of n and k are 0.28 and 0.22 respectively. Q_{ext} for this case is given by (12)

$$Q_{avt} = 1.57X + 9.85X^{4}$$
 , $X < 0.3$ [15]

For gold particles used in this experiment, $\overline{a} = 5 \text{ nm}$ and $\lambda = 633 \text{ nm}$, therefore X = 0.05 < 0.3. Hence Eq. [13] can be used to calculate Q_{ext} of the gold particles.

Light transmittance intensity through a water/silicone oil emulsion where the water contains 50 g gold per liter is ~ 0.36. Therefore all log normal radius distributions which give $(I_t/I_o)_{exp}$ between 0.3 and 0.4 were The resulting distributions representing points a, b and c are searched. listed in Table 2. The calculations of α_c were done for point d, listed in Table 2, which also corresponds to $(\overline{a}, \sigma) = (0.2 \ \mu m, 0.36)$. These values of α_{c} are compared to the case where the emulsion is pure water/silicone oil in Fig. 16. The results show that the coalescence efficiency coefficient in the presence of gold is smaller than the pure water case. The reason for this is that the gold particles migrate to the water oil interface (measured contact angle for the system water/silicone oil/gold is $66^{\circ} \pm 2^{\circ}$) due to Brownian motion or due to possible attraction forces between the gold particles and the water/oil interface. At the interface, gold particles prevent the water droplets from coming closer than a distance in the order of their diameter, hence they prevent the droplets from coalescence.

Fig. 16 The coalescence efficiency coefficient versus Gt for water/silicone oil and water contains 50 g gold particles/L - silicone oil emulsions sheared at 10 s⁻¹. The calculations were done for C = 1.0 and $a_c = 2.0 \ \mu m$.



Besides, the water droplets experience an additional repulsive force due to the repulsion forces between gold particles in every droplet. These two reasons result in a lower value of the coalescence efficiency.

Similar results were found by Thompson et al. (13). They found that the presence of waxes and associated solids in crude oil exerted considerable stability upon the emulsion. They also found that removing these solids by heating or by centrifugation decreases considerably the stability of the emulsion. They also stated that the radius of the solid particles plays an important role in the stability of the emulsion. In fact the above observation is called the "Pickering" effect, studied in detail by Levin et al (14).

CONCLUDING REMARKS

Shear forces, hydrodynamic resistance, and the ratio of the van der Waals attractive forces to that of the interfacial tension forces play an important role in the stability of an emulsion. Changing any of these forces results in a different degree of emulsion stability. These forces can be altered by altering the shear rate or adding additives to the emulsions. The effects of the shear rate and the additives were studied. The following tentative conclusions can be drawn:

- Lowering the interfacial tension stabilizes the water/oil emulsions. This can be achieved by adding surfactants or electrolytes to the water phase.
- 2. In the presence of shear, the emulsions are least stable at intermediate shear rates, similar to hard sphere dispersions. However for

water droplets in oil, the repulsive force arises mainly from drop deformation rather than electrostatic repulsion.

3. The effect of solid particles at the water/oil interface was also tested. The results showed that solid particles increase the emulsion stability, similar to an oil/water emulsion.

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NOMENCLATURE

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a	- radius of the droplets, m.
A	- Hamaker constant, J.
С	- arbitrary parameter, dimensionless.
C _(r,q)	- correction factor to Stoke's law, dimensionless.
E, , E ₂	- arbitrary numbers, dimensionless.
F	- force, N.
g(r,q)	- function of r and q, dimensionless.
G	- shear rate, s^{-1} .
It/I°	- ratio of the transmitted light to that of the incident light,
	dimensionless.
К	 imaginary part of the refractive index, dimensionless.
m	- ratio of the refractive index of the particles to that of the
	continuous media, dimensionless.
n	 real part of the refractive index, dimensionless.
Р	 probability distribution function, dimensionless.
q	- ratio of the radius of the colliding droplets, dimensionless.
Q	- scattering efficiency, dimensionless.
t	- time, S.
u	- velocity, m s ⁻¹ .
X	- dimensionless variable defined in Eq. 14.
Z	- parameter defined by Eq. 14.
Greek	
α	- coalescence efficiency, dimensionless.
ε	 permittivity of free space, Farad/m.

- λ wavelength of the light, μ m.
- γ interfacial tension, N m⁻¹.
- ρ density, kg m⁻³.

Scripts

1 - path length that light travels, m.

Superscripts

- used to define a dimensionless parameter.
- - used to define average value of a parameter.

Subscript

c - coefficient of

exp

- used to define the experimentally measured value of a parameter. CHAPTER 5

SHEAR INDUCED COALESCENCE OF WATER IN OIL EMULSION DROPLETS SIMULATED BY A MONTE CARLO METHOD

ABSTRACT

Simulation of shear-induced coalescence of emulsion droplets by a Monte Carlo method is described. The approach is based on generating a droplet from a given droplet radius distribution and a second droplet from the corresponding frequency distribution. A collision is considered successful if a generated random number is smaller than the orthokinetic coalescence efficiency coefficient, which is assumed to be a function of the radius ratio of the colliding droplets.

The self-preserving form hypothesis was tested. It was found that the radius distribution of the emulsions that were examined is self-preserved.

INTRODUCTION

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There are a countless number of papers in the literature dealing with Brownian- and shear-induced coagulation of colloidal particles. Whether these investigations were experimental, theoretical or both, most of them had to deal with a numerical solution of Smoluchowski's coalescence equation. For monodisperse and uniform distributions of particles, the numerical solution of Smoluchowski's equation presents no problems and the needed amount of computing memory is not excessive. However, the computation time and memory grow larger as coagulation proceeds, since the distribution becomes more polydisperse. Besides the increase in polydispersity, the solution becomes inadequate for long coagulation times.

Many attempts have been made to resolve these problems. Kobraei and Duncan (1) suggested two approximations (infinite tail approximation and polynomial solution) to avoid long computation time and memory. In the depletion of term kernel in the approximation, the polynomial Smoluchowski's equation is approximated by a constant value. This approximation gives accurate results if and only if the fluctuation of the kernel around its average value is small. In the infinite tail approximation, however, they assumed that the kernel in the depletion term is constant from a certain point in the distribution to infinity. They claim that these approximations are remarkably accurate for long coagulation times. Assuming that the distribution can be divided into classes whose radii are related by $a_i = a_0(i)^{1/3}$, where a_0 is the minimum radius of the distribution, Suzuki, Ho and Higuchi (2) studied the particle radius distribution changes in emulsions and suspensions. In their

analysis they avoided long computation times and large memory by Simon (3) showed that a arbitrarily choosing a maximum value of i. separable particular solution exists for the coagulation equation if a source term exists with a time variation of the form $(t_0 - t)^{-2}$. In his mathematical analysis, Simon assumed that the source term and the particle radius distribution were both separable functions of volume and time. Mulholland and Mountain (4) numerically studied the applicability of Smoluchowski's equation with a constant kernel to coalescence. Their analysis is valid only for short coalescence times before complicating effects due to droplet coalescence become important. They modified Smoluchowski's Brownian coagulation equation by including a transient term in which a self diffusion constant of the particles was used. In their comments on Mulholland and Mountain's paper, Marqusee and Mulholland (5) suggested that the self diffusion constant is inappropriate to use and a better agreement with the direct solution of Smoluchowski's equation can be attained by replacing it with a relative diffusion constant. Williams (6) and Warszynski and Czarnecki (7) showed that coagulation kinetics can be described by a set of approximate equations for time evolution of moments. They stated that the results of the moments method agree very well with those obtained from direct solution of Smoluchowski's equation and that the method reduces the computation time by two orders of magnitude.

In this paper we follow the time evolution of emulsion droplets in simple shear by using Monte Carlo simulation (8-12). This method eliminates the need for huge computer memory that forced people working on this problem to limit their analysis to a certain radius. It also eliminates the worry about the adequacy of the solution of Smoluchowski's equation at

long coagulation time. Moreover, it requires much less computation time compared to the direct solution of Smoluchowski's equation and it has the advantage that it is more accurate and can be used for an arbitrary dependence of the coalescence efficiency on radius ratio, particle size and other variables.

THEORETICAL ANALYSIS

Consider an emulsion whose initial droplet radius distribution is divided into classes as shown in Fig. 1. Let us randomly choose a droplet from class i of radius a_i . Upon shearing the emulsion, this droplet, in essence, can collide with any other droplet in the emulsion. The collision frequency of a droplet from class i with any class j whose number of droplets per unit volume is n_i is given by Smoluchowski (13) as

$$F_{ij} = \frac{4G}{3} \sum_{j=1}^{N} (a_i + a_j)^3 n_j .$$
 [1]

If the number of droplets in class i is n_i then the collision frequency between class i and j is

$$F = \frac{4G}{3} \sum_{i=1}^{N} \sum_{j=1}^{N} (a_i + a_j)^3 n_i n_j , \qquad [2]$$

where G is the shear rate and I is the total number of classes the distribution has. Fig. 1 Initial log normal droplet radius distribution divided into classes. The mean radius and the standard deviation are 0.3 μ m and 0.35, respectively.

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Plotting the collision frequency, F_{ij} versus a_j will give a frequency distribution function, as can be seen in Fig. 2, for the case where G = 10 s^{-1} , and for a log normal distribution with mean radius $\bar{a} = 0.3 \ \mu m$ and a standard deviation $\sigma = 0.35$. This distribution will be skewed to the left compared to the radius distribution because n_j is multiplied by a_j^3 , as can be seen from Eq. [1]. The probability that a droplet i will collide with another droplet k is proportional to F_{ik} . Therefore a droplet k randomly chosen from the frequency distribution function is allowed to collide with droplet i. The collision efficiency between droplet i and droplet k is related to their radius ratio, as discussed in Chapters 3 and 4. An approximate expression is given by the following equation

$$\alpha_{ik} = \alpha_{c} \left\{ \begin{bmatrix} \frac{4q_{ik}}{(1+q_{ik})^{2}} \end{bmatrix}^{C} , a \leq a_{c} \\ 0, a , a > a_{c} \end{bmatrix}$$
[3]

where α_{c} is the orthokinetic coalescence efficiency coefficient, $q_{ik} = a_{i}/a_{k}$, is the radius ratio of the colliding droplets, a_{c} is a critical radius above which $\alpha_{ik} = 0$ and C is an exponent whose value, in general varies from 1 to 6. As discussed in Chapter 3, the dependence of α_{c} on C. ranging from 1 to 6 varies within $\pm 2\%$. Therefore a value of C = 5 was used.

After α_{ik} is calculated, a random number R is generated via a random number generator (14). The values of R vary between 0 and 1. If R > α_{ik} then the collision is considered inefficient, i.e. the collision does not lead to coalescence, otherwise the collision is efficient and coalescence

Fig. 2 The collision frequency, F_{ij} between a droplet of radius a_i and droplet in class j calculated by Eq. [1]. The droplet radius distribution is log normal $\overline{a} = 0.3 \ \mu m$ and $\sigma = 0.35$. The value of $a_i = 0.345 \ \mu m$.

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between droplet i and droplet k occurs. If the collision is inefficient then another droplet i is chosen and the above procedures are repeated. If the collision is efficient then the number of droplets in class i and class k will be less by one droplet each and class i + k, provided that $V_i + V_k =$ V_{i+k} , where V is the volume, will increase by one droplet. Another droplet i is chosen and the above steps are repeated. Since the number of collisions (the number of times a droplet i is created) is proportional to the shearing time, the above steps are repeated until a desired shearing time is achieved or the total number of droplets has fallen to a required value. The above procedures are summarized below:

- 1. From a known initial droplet radius distribution, a droplet from class i whose radius and volume are a_i and V_i is randomly chosen.
- The collision frequency of this droplet with other droplets is calculated from Eq. [1]. Hence a frequency distribution function is obtained.
- 3. A droplet from class k of the frequency distribution function whose radius and volume are a_k and V_k is also randomly selected and allowed to collide with droplet i.
- 4. The orthokinetic coalescence efficiency is then calculated from Eq. [3].
- 5. A random number R ($0 \le R \le 1$) is generated. If $R > \alpha_{ik}$ then the collision is inefficient. If $R < \alpha_{ik}$ then the collision is successful and coalescence between i and k takes place.
- 6. If the collision is inefficient then steps 1 through 5 are repeated for another collision. If the collision is successful then

$$n_{i} = n_{i} - 1$$

$$n_{k} = n_{k} - 1$$

$$n_{i+k} = n_{i+k} + 1, \text{ provided that } V_{i} + V_{k} = V_{i+k}$$

7. Procedures 1 through 6 are repeated for another collision and so on.

It should be pointed out that when a successful collision takes place the distribution is changed and, therefore, new classes appear. Whenever the above procedures are repeated the change in the droplet radius distribution, and hence the frequency distribution, should be taken into account. The subroutine MOCARLO, which was used to carry out the above simulation procedures, is shown in Appendix 5-A.

Generation of a Random Droplet

If the droplet radius distribution shown in Fig. 1 is replotted as a cumulative radius distribution, \sum_{i} / N_{t} , versus a_{i} , then the result will be as shown in Fig. 3. The cumulative size distribution will vary from 0 to 1. Generating a random number, R will also have a value ranging from 0 to 1. The value of the random number is read from the y axis of Fig. 3. A straight line from R parallel to the x axis will intersect the cumulative curve at a point P. The location of point P on the cumulative curve will determine the class from which a droplet should be chosen. If this way of randomly choosing a droplet is correct, then one should be able to regenerate the droplet radius distribution. In Fig. 4 the initial droplet radius distribution generated by the above method shown by a solid line. A thousand random numbers were used for this purpose. One can see from Figs. 3 and 4 that this

Fig. 3 The cumulative droplet radius distribution for the log normal distribution given in Fig. 1. A point P on the figure determines a random choice of class i.



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Fig. 4 The initial droplet radius distribution given in Fig. 1, shown by open circles, is compared to a randomly obtained distribution, shown by the solid line. 1000 random classes were used to regenerate the initial distribution.

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method is an accurate way of choosing a random droplet from a given droplet radius distribution.

The same procedures were followed to choose a droplet from the frequency distribution function. In this case the frequency F_{ik} was normalized by dividing it by F and the random number R ranges between zero and $\Sigma F_{ik}/F$.

RESULTS AND DISCUSSION

As the number of collisions proceed, and hence the shearing time, the droplet radius distribution changes. Due to coalescence the number of droplets decreases in some classes and increases in others. The larger the number of collisions, the larger the change in the droplet radius distribution. To relate the number of collisions to the different parameters of the system we define the following parameters. Let χ be the number of collisions the computer generates and F_o be Smoluchowski's collision frequency at time t = 0. A dimensionless parameter η can be defined as

$$\eta = \frac{\chi N_o G \alpha_c}{F_o} , \qquad [4]$$

where N is the total number of droplets at time t = 0. The shearing time is related to η by the following equation:

$$t = \frac{N_t \chi}{F_t} = \frac{\eta}{G\alpha_c}, \qquad [5]$$

where N_t and F_t are the total number of droplets and collision frequency at any time t.

Fig. 5 shows the change in an initially log normally distributed emulsion with $\overline{a} = 0.3 \ \mu m$ and $\sigma = 0.35$. The values of C, α_c and α_c were chosen to be 5.0, 1.0 and 2.0 μm , respectively. It can be seen from Fig. 5 that as η increases, the shearing time and the number of droplets, of which size there are many, change faster than those for which the number concentration is low. The reason for this is that the probability of choosing a droplet from the former is higher than the latter. Hence the former decreases more rapidly than the latter. In fact, the classes which contain a small number of droplets and whose radius is larger than 0.48 μm increase their number of droplets with time due to the coalescence of smaller droplets. Whereas droplets below 0.16 μm show no change because either there are no smaller droplets which give rise to them, or the chance for them to coalesce with others is very low since the coalescence efficiency is too small.

The effect of the parameter C on the change of the distribution was tested. For this purpose, values of C ranging from 0 to 100 were examined. The change in the droplet radius distribution for the case where C = 0 is shown in Fig. 6. A value of C = 0 means that $\alpha = 1$ and thus all collisions are efficient and lead to coalescence. The rate of depletion of droplets whose number is large is faster for C = 0 than for C = 5. The change in the total number of droplets plotted as $N^* = (N_o - N_t)/N_o$ versus C for various values of η is shown in Fig. 7. The following can be observed from this figure. First of all, as $C \to \infty$, $N^* \to 0$. Secondly, as $C \to 0$, N^*

Fig. 5 Changes in the droplet radius distribution as collisions proceed. The values of \overline{a} , σ , a_c and C are 0.3 μ m, 0.35, 2.0 μ m and 5, respectively.

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Fig. 6 Changes in the initial droplet radius distribution as collisions proceed. The values of \overline{a} , σ , a_c and C are 0.3 μ m, 0.35, 2.0 μ m and 0, respectively.

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a (µm)
Fig. 7 The change in $(N_o - N_t)/N_o$ versus C for various values of η . The droplet radius distribution is as given in Fig. 1.

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attains a certain value which is a function of η and, finally, as $\eta \to 0$ for any value of C, N* $\to 0$. The above observations can be described by the following formula which describes N* as a function of C and η

$$N^* = (1 - e^{-k_1} \eta) e^{-k_2 \sqrt{C}} .$$
 [6a]

The values of N* obtained from the numerical results obtained by the above method are fitted to the above equation from which the values of the constants k_1 and k_2 were found to be $(4.35 \pm 0.01) \times 10^{-10}$ and 0.150 ± 0.004 , respectively. For the case where N* changes by < 10% the above equation can be replaced by

$$N^* = k_4 \eta e^{-k_2 \sqrt{C}} , \qquad [6b]$$

where k_4 is $(4.19 \pm 0.01) \times 10^{-10}$ and k_2 has the same value as above.

The effect of polydispersity was also investigated. A log normal distribution with a value of $\sigma = 0.6$ was chosen. The mean radius is kept the same as in the previous test (0.3 μ m). The change in the droplet radius distribution is portrayed in Fig. 8.

The change in the total number of droplets as the number of collisions increases was calculated by the Monte Carlo simulation and by numerically solving the coagulation equation of Smoluchowski (13). The results of N_t/N_o versus F_t/F_o are depicted in Fig. 9. F_t/F_o is the ratio of the collision frequency calculated from Eq. [2] at any time t to the collision

Fig. 8 Changes in the initial droplet radius distribution as collisions proceed. The values of \overline{a} , σ , a_c and C are 0.3 μ m, 0.6, 2.0 μ m, and 5, respectively.



Fig. 9 Comparison between N_t/N_o versus F_t/F_o obtained by direct solution of Smoluchowski's equation and Monte Carlo method.

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frequency at t = 0. The slope of N_t/N_o versus F_t/F_o for the direct solution of Smoluchowski's equation and the Monte Carlo simulation are 0.76 and 0.94, respectively. A comment must be made here about the comparison that is shown in Fig. 9. The slopes of the Monte Carlo and the numerical solutions of Smoluchowski's equation seem to be different by ~ 20%. Actually, it was noticed that the slope is extremely sensitive to the numerical solution of the coagulation equation. The slope ($\Delta N/\Delta F_t$) of Smoluchowski is

$$\frac{1.0 - 0.987}{1.0 - 0.983} = 0.76$$

whereas the slope of the Monte Carlo is

$$\frac{1.0 - 0.985}{1.0 - 0.984} = 0.94$$
.

This shows how sensitive the slopes are to the numerical solution of Smoluchowski's equation. In the numerical solution of Smoluchowski's equation, the classes were divided according to $a_i = (xi)^{1/3}$ where x = 5.0 was chosen. Because of the finite memory of the computer and the computation time limitation, a smaller value of x could not be tried. Therefore improvement of the above result can still be done at the expense of increasing the computer time. From this one can conclude that the results of the Monte Carlo method are much more accurate than that of the results of the numerical solution of Smoluchowski's equation.

In the previous chapter the coalescence efficiency was calculated from experimental data using the numerical solution of Smoluchowski's set of

differential equations. Calculating α_c from Monte Carlo simulations instead results in a difference of about 5%, well below the experimental error of about 8%.

SELF-PRESERVING FORM DISTRIBUTIONS

Rajagopal (15) showed that the course of the coalescence process can be described by the time variation of a droplet radius distribution. Swift and Friedlander (16) extended Rajagopal's idea and used a mathematical procedure called "similarity transformation" to solve the full shear coalescence equation of Smoluchowski, the similarity transformation method transforms Smoluchowski's equation to a total differential equation. Swift and Friedlander also proposed a self-preserving hypothesis written in the form, where V is the volume and N_t is the total number of droplets per unit volume,

$$p(V,t) = \frac{N_t^2}{\phi} \psi(VN_t/\phi) , \qquad [7]$$

and showed that Eq. [7] is a solution of the similarity transformed form of Smoluchowski's equation. In Eq. [7] p(V,t) is the probability distribution function and ϕ is the volume fraction. The mathematical analysis of the similarity transformation will not be shown here, but the reader is referred to the original paper by Swift and Friedlander.

The results of the similarity transformation hypothesis indicate that if the cumulative fraction of particles, $\Sigma n_i / N_t$, $(1 - \Sigma (n_i / N_t))$ in Swift and Friedlander's work) is plotted against the dimensionless parameter $\xi = VN_t/\phi$ and if the plot gives a unique curve then the distribution is self-preserved.

Ali and Zollars (17) examined the self-preserving particle radius distribution hypothesis during shear coagulation. They concluded that the particle size distribution that evolves during shear coagulation appears to be a self-preserving distribution. They also concluded that "claims that the shear coagulation of dispersions with good Brownian stability does not yield self-preserving distributions are in error and a distribution is a self-preserved one as long as the coagulation process is dominated by shear coagulation whether the initial distribution is stable to Brownian coagulation or not". A similar conclusion was obtained by Meesters and Ernst (18), who numerically evaluated the self-preserving form in Smoluchowski's coagulation equation.

In this chapter we plot the cumulative radius distribution as a function of ξ to check the self-preserving hypothesis put forward by Swift and Friedlander. The results are depicted in Fig. 10 where $\Sigma(n_i/N_t)$ is plotted versus ξ and η as a parameter. The values of C, \bar{a} and σ that are used to calculate the change in the total number of droplets are 5.0, 0.3 μ m and 0.35, respectively. It can be seen that the self-preserving hypothesis is satisfied during the coalescence process. A similar plot was obtained for the case where C = 5.0, $\bar{a} = 0.3 \ \mu$ m and $\sigma = 0.6$. The results are shown in Fig. 11. It should be noted that the same plots are valid for any value of C since the initial radius distributions are the same in both cases.

Fig. 10 The cumulative droplet radius distribution given in Fig. 1 versus ξ for all values of η . The results are applicable for any value of C. The difference is within the thickness of the line. The figure shows that the distribution is self-preserved.



(

Fig. 11 The log normal cumulative droplet radius distribution of $\overline{a} = 0.3$ μm and $\sigma = 0.6$ versus ξ for all values of η and C. The difference is within the thickness of the line. The self-preserving form can be seen from the above curves.



CONCLUSIONS

An approach to simulate shear-induced coalescence of emulsion droplets by Monte Carlo simulation has been described. The evolution of the droplet radius distribution, the change in the total number of droplets and the collision frequencies were calculated. Comparison of these results with those obtained from numerical solution of Smoluchowski's equation was performed. It was found that the results are very sensitive to the numerical solution of Smoluchowski's equation. The effect of the parameter C on the evolution of the droplets was examined.

The self-preserving form distribution hypothesis was tested. It was found that the distributions that were tested in this chapter satisfy the self-preserving form hypothesis.

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NOMENCLATURE

a	- droplet radius, μm.
С	- exponent parameter, dimensionless.
F	- collision frequency, $m^{-3}s^{-1}$.
G	- shear rate, s ⁻¹ .
n	- number of droplets per unit volume, m^{-3} .
N	- total number of droplets per unit volume, m^{-3} .
р	 probability distribution function, dimensionless.
q	- droplets radii ratio, dimensionless.
t	- time, s.
v	- droplet volulme, m ³ .
Greek	
α	 orthokinetic coalescence efficiency, dimensionless.
χ	 number of collisions which the computer generates.
φ	- volume fraction, dimensionless.

-

- η parameter given in Eq. [4], dimensionless.
- ξ ratio of droplet volume to the average droplet volume, dimensionless.

APPENDIX 5-A

THE SUBROUTINE MOCARLO THAT SIMULATES THE SHEAR INDUCED COALESCENCE OF EMULSION DROPLETS BY A MONTE-CARLO METHOD

SUBROUTINE MOCARLO

C C COLLESCENCE PROCESS BETWEEN
C TWO EMULSION DROPLETS. FIRSTLY, IT DIVIDES ANY GIVEN
C LOG NORMAL DISTRIBUTION INTO CLASSES AND THEN II
C CALCULATES THE NUMBER OF DROPLETS IN EACH CHASES A
C SECONDLY, FROM A CERTAIN CLASS IT INTERPOLENCY BETWEEN
C DROPLET AND CALCOLATES THE COLLECTION OF THE CLASSES. FINALLY, IT
C THIS DROPLET AND THE FREQUENCY DISTRIBUTION.
C A RANDOM NUMBER R IS GENERATED. IF RCALPHA THEN THE
C COLLISION IS EFFICIENT AND COALESCENCE OCCORD OTHER
C THE COLLISION DOES NOT LEAD TO COALDOLLOU THE
C ABOVE PROCEDURE SHOULD BE KILLENTED
C TE THE COLLISION IS EFFICIENT THEN EACH OF THE ABOVE
C CHOSEN CLASSES LOOSE A DROPLET EACH AND THE CLASS WHOSE
C VOLUME IS EQUAL TO THE VOLUIME OF THE ABOVE CLASSES
C GAINS A DROPLET. THE ABOVE PROCEDURES ARE REPEATED THIS
C SO ON.
C
C THIS SUBROUTINE CHEEC CHE
C 1. SUBROUTINE LOGNORM TO DIVIDE THE LOG NORMAL
C DISTRIBUTION INTO CLASSES AND CALCULATES THE
C NUMBER OF DROPLETS IN EACH CLASS. THE
C INTERN CALLS SUBROUTINE ENGLAND
C ERROR FUNCTION.
C 2. SUBROUTINE MISCAT TO CALCULATE THE LIGHT
C SCATTERING EFFICIENCY.
C DETERMINE TO WHICH CLASS A
C 3. SUBROUTINE DET TO DETERMINE TO WHICH CLIEBER SIZE
C RANDOMLY GENERATED NOMBER & DEET
C DISTRIBUTION:
C 4. SUBROUTINE DETFREQ TO DETERMINE TO WHICH CLASS A
C RANDOMLY GENERATED NUMBER R BELONG IN THE
C FREQUENCY DISTRIBUTION.
C CENERATE A RANDOM NUMBER R
C 5. SUBROUTINE RANT TO GENERATE SUBROUTINE WAS
C COPIED FROM REFERENCE 14 IN CHAPTER 5.
C THIS SUBROUTINE REQUIRES THE FFOLLOWING DATA AS INFOL
C DISTRIBUTION.
C 1. AM=MEAN RADIUS OF THE LOG RORALD DEPENDENT
C
C DISTRIBUTION.

```
3. C=THE VALUE OF THE EXPONENT APPERS IN EQN. [3] IN
С
С
         CHAPTER 5.
С
С
С
      COMMON /CMAX/JCLASS,K1,SUM(2001),SUMFREQ(2001)
      COMMON/SCAT/AP(2001), QZ(2001), FREQ(2001), TN, JCLASS
      DIMENSION QSCA(2001)
С
C****** INITIATION SECTION *****
С
      AM=0.3
      SIG=0.35
      C=5.0
      ALFAC=1.0
      W=1.0/3.0
       PI=3.1415927
       AP(1) = .015
       PEOFPA=0.999
       IDUM=0
       NTOTAL=0
       YINIT=RAN1(IDUM)
       DO 988 IA= 2,2000
       AP(IA) = AP(IA-1) + .03
   988 CONTINUE
       CALL LOGNORM (SIG, AM, PEOFPA)
       CALL MISCAT
 С
 C CALCULATE THE COLLISION FREQUENCY AT TIME=0.0
 С
       SMOL=0.0
       DO 5 L6=1, JCLASS
       DO 5 L7=1, JCLASS
       SMOL=SMOL+QZ(L7)*QZ(L6)*((AP(L7)+AP(L6))**3)
       CONTINUE
   5
       SMOL=SMOL*4.0*1.0E-9/3.0
       NTRIAL=NUMBER OF COLLISIONS ONE WOULD LIKE TO CREATE
 С
 С
 С
 C IPRINT IS CHOSEN TO PRINT DATA AFTER IPRINT NUMBER OF
 C COLLISIONS.
 С
        TUR=0.0
        DO 7 L9=1, JCLASS
        TUR=TUR+QSCA(L9)*QZ(L9)*AP(L9)**2
      7 CONTINUE
        TRANS=EXP(-PI*2.3*TUR*1.0E-6)
        DO 1 I=1,NTRIAL
        IF (MOD(I, IPRINT) .NE. 0) GO TO 8
        TUR=0.0
        DO 15 L10=1, JCLASS
```

```
203
```

```
TUR=TUR+QSCA(L10)*QZ(L10)*AP(L10)**2
  15 CONTINUE
     TRANS=EXP(-PI*2.3*TUR*1.0E-6)
      FEQ=0.0
      DO 48 L11=1, JCLASS
      DO 48 L12=1, JCLASS
      FEQ=FEQ+4.0*QZ(L11)*QZ(L12)*((AP(L11)+
     +AP(L12))**3)/3.0
   48 CONTINUE
С
C GENERATING A RANDOM DROPLET FROM THE INITIAL DISTRIBUTION
С
    8 P1=RAN1(IDUM)
C
C CALL SUBROUTINE DET TO DETERMINE TO WHICH CLASS THIS
C DROPLET BELONG
С
      CALL DET(P1)
      KA = K1
С
C IF THE DROPLET BELONG TO A CLASS WHICH IS ALREADY
C DEPLETED THEN CREATE ANOTHER DROPLET
С
      IF (QZ(KA) .LE. 0.0) GO TO 8
      SIZE1=AP(KA)
С
C CALCULATE THE FREQUANCY AT WHICH THE ALREADY CHOSEN
C DROPLET COLLIDE WITH THE OTHER EXISTING DROPLETS =
C 4*QZ(J)*1.0*(SIZE1+AP(J))**3/3.0
С
      DO 9 KK=1, JCLASS
      FREQ(KK)=(4.0*QZ(KK)*(SIZE1+AP(KK))**3)/3.0
      IF (KK .EQ. 1) SUMFREQ(1)=FREQ(1)
      IF (KK .NE. 1) SUMFREQ(KK)=SUMFREQ(KK-1)+FREQ(KK)
       CONTINUE
   9
       P2=SUMFREQ(JCLASS) *RAN1(IDUM)
   6
       CALL DETFREQ(P2)
       KB=K1
       IF (QZ(KB) .LE. 0.0) GO TO 6
       SIZE2=AP(KB)
   22 QIJ=SIZE1/SIZE2
       ALFA=ALFAC*(4.0*QIJ/((1.0+QIJ)**2))**C
       IF((SIZE1 .GT. 2.0) .OR. (SIZE2 .GT. 2.0)) GO TO 1
 С
 C IF CHANCE < ALFA THEN THE COLLISION IS SUCCESSFULL HENCE
 C CREATE ANOTHE ORIGINAL DROPLET, IF NOT CREATE ANOTHER
 C DROPLET
 С
       CHANCE=RAN1 (IDUM)
       IF (CHANCE .GT. ALFA) GO TO 1
       NSUC=NSUC+1
```

```
204
```

```
QZ(KA) = QZ(KA) - 1.0
      QZ(KB) = QZ(KB) - 1.0
      ASIZE=((AP(KA)**3)+(AP(KB)**3))**W
      HK=0.0
      DO 43 L3=1, JCLASS
      HK=HK+.03
      IF (ASIZE .LT. HK) GO TO 44
   43 CONTINUE
   44 QZ(L3) = QZ(L3) + 1.0
      TN=0.0
      DO 2 L1=1, JCLASS
      TN=TN+QZ(L1)
  2
      CONTINUE
      SUM(1) = QZ(1) / TN
      DO 3 L2=2, JCLASS
      SUM(L2) = SUM(L2-1) + QZ(L2) / TN
  3
      CONTINUE
      CONTINUE
  1
      RETURN
      END
С
C *** SUBROUTINE DETERMIN ***
С
      SUBROUTINE DET(PP)
      COMMON /CMAX/JCLASS, K1, SUM(2001), SUMFREQ(2001)
      DO 2 I1=1, JCLASS
      A=SUM(I1)
      IF (A .LT. PP) GO TO 2
      K1=I1
      RETURN
  2
      CONTINUE
      K1=JCLASS
      RETURN
      END
C
C *** SUBROUTINE TO CHOOSE A PARTICLE FROM THE FREQUANCY
C DIDTRIBUTION
С
      SUBROUTINE DETFREQ(PP)
      COMMON /CMAX/JCLASS, K1, SUM(2001), SUMFREQ(2001)
      DO 3 I1=1, JCLASS
      A=SUMFREQ(I1)
      IF (A .LT. PP) GO TO 3
      K1=I1
      RETURN
      CONTINUE
   3
      K1=I1
      RETURN
      END
С
C *** FUNCTION SUBPROGRAM TO GENERATE A RANDOM NUMBER ***
```

С

```
FUNCTION RAN1 (IDUM)
     DIMENSION R(97)
     PARAMETER (M1=259200, IA1=7141, IC1=54773,
    +RM1=3.8580247E-6)
     PARAMETER (M2=134456, IA2=8121, IC2=28411,
    +RM2=7.4373773E-6)
     PARAMETER (M3=243000, IA3=4561, IC3=51349)
     DATA IFF /0/
     IF (IDUM.LT.O.OR.IFF.EQ.0) THEN
     IFF=1
     IX1=MOD(IC1-IDUM, M1)
     IX1=MOD(IA1*IX1+IC1,M1)
     IX2=MOD(IX1,M2)
     IX1=MOD(IA1*IX1+IC1,M1)
     IX3=MOD(IX1,M3)
     DO 11 J=1,97
     IX1=MOD(IA1*IX1+IC1,M1)
     IX2=MOD(IA2*IX2+IC2,M2)
     R(J) = (FLOAT(IX1) + FLOAT(IX2) * RM2) * RM1
11
     CONTINUE
     IDUM=1
     ENDIF
     IX1=MOD(IA1*IX1+IC1,M1)
     IX2=MOD(IA2*IX2+IC2,M2)
     IX3=MOD(IA3*IX3+IC3,M3)
     J=1+(97*IX3)/M3
     IF (J.GT.97.OR.J.LT.1) PAUSE
     RAN1=R(J)
     R(J) = (FLOAT(IX1) + FLOAT(IX2) * RM2) * RM1
     RETURN
     END
```

CHAPTER 6

GENERAL CONCLUSIONS

CONCLUSIONS

The following are certain observations and conclusions that summarize the research described in this thesis.

- The particle radius distributions of colloidal systems of various degrees of polydispersity can be determined from light transmittance measurements at various wavelengths of light.
- The orthokinetic coalescence efficiency between emulsion droplets in simple shear flow can be estimated by comparing experimentally measured and theoretically calculated light transmittance intensities.
- 3. The orthokinetic coalescence efficiency, for a given system, depends on the colliding droplets radius ratio and their surface potential and can be expressed approximately in the form given by Eq. [11] in Chapter 3.
- 4. Changing any of the following: surface potential, interfacial tension and shear rate, alters the orthokinetic coalescence efficiency.
- 5. Adding electrolytes to the water phase of the emulsion results in a more stable emulsion in a certain shear rate range and a less stable emulsion in some other range of the shear rate. The higher degree of stability can be mainly attributed to a lowering of the interfacial tension.
- 6. When the interfacial tension decreases, indicating that the droplets can be more readily deformed, the orthokinetic coalescence efficiency decreases and, hence, the emulsion becomes more stable.
- 7. The presence of solid particles at the water/oil interface decreases the orthokinetic coalescence efficiency and thus stabilizes the emul-

sion.

- 8. The orthokinetic coalescence efficiency as a function of shear rate goes through a minimum and a maximum consecutively.
- 9. It is possible to simulate the coalescence of the emulsion droplets by a Monte Carlo method. This has the advantage of eliminating huge computer memory and decreases considerably the time that is needed for the solution of Smoluchowski's coagulation equation.
- 10. Applying Monte Carlo simulation to shear-induced coalescence overcomes the problems that arise from numerically solving Smoluchowski's coagulation equation.
- 11. Plotting the results presented in special dimensinless form $\sum_{i} N_{t}$ versus $\xi = VN_{t}/\phi$, shows that the distributions studied theoretically in this thesis are of the self-preserving form.

CLAIMS FOR ORIGINAL RESEARCH

We believe that the following are original contributions made by this research:

- A quick, accurate and simple method to determine the particle radius distributions of colloidal systems of various ranges of polydispersity has been developed.
- A method to estimate the orthokinetic coalescence efficiency has been developed.
- 3. An equation describing the dependence of the orthokinetic coalescence efficiency on the colliding droplets radius ratio and their surface potentials has been proposed.

- 4. The effects of the shear rate, presence of solid particles at the water oil interfaces, electrolytes, surface active agents and interfacial tension on the orthokinetic coalescence efficiency has been investigated. This is the first experimental study to determine the effects of various additives on the orthokinetic coalescence efficiency.
- 5. The shear-induced coalescence of emulsion droplets has been simulated using a new Monte Carlo method.

RECOMMENDATIONS FOR FUTURE WORK

The dependence of the orthokinetic coalescence efficiency on the colliding droplets radius ratio was given in Eq. [11], Chapter 3. This equation has three parameters. Determining these parameters with a polydisperse system is a very difficult task. Therefore it is recommended to develop a method to produce monodisperse emulsions. This study will not only be useful to colloid scientsits, but it is also of great importance to biotechnologists. A technique to do this is already available in (1), but the rate of droplets produced by the method explained in (1) is very small compared to the number of emulsions droplets necessary in most applications.

Doing this would enable one to check the importance of every parameter and its effect on the orthokinetic coalescence efficiency.

The rheology of emulsions has been investigated by many authors (2,3). The effect that coalescence of emulsion droplets has on the rheological properties of the emulsions have not been investigated thoroughly. There-

fore it is necessary to study this area in more detail, especially the many body interaction terms that appear in the statistical mechanical theory for viscosity.

In the microcouette apparatus shear rates higher than 250 s^{-1} were not possible to apply due to some design problems. A modification of the design such that higher shear rates can be applied is recommended.

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