

EVALUATING THE DLVO MODEL FOR NON-AQUEOUS COLLOIDAL
SUSPENSIONS

BY

KEITH JOSEPH DECARLO

A THESIS

SUBMITTED TO THE FACULTY OF

ALFRED UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CERAMICS

ALFRED, NEW YORK

MAY, 2011

Alfred University theses are copyright protected and may be used for education or personal research only. Reproduction or distribution in any format is prohibited without written permission from the author.

EVALUATING THE DLVO MODEL FOR NON-AQUEOUS COLLOIDAL
SUSPENSIONS

BY

KEITH JOSEPH DECARLO

B.S. ALFRED UNIVERSITY (2006)

M.S. ALFRED UNIVERSITY (2008)

SIGNATURE OF AUTHOR _____ (Signature on File)

APPROVED BY _____ (Signature on File)
WILLIAM CARTY, ADVISOR

(Signature on File)
ANDREW EKLUND, ADVISORY COMMITTEE

(Signature on File)
MATTHEW HALL, ADVISORY COMMITTEE

(Signature on File)
VASANTHA AMARAKOON, ADVISORY COMMITTEE

(Signature on File)
CHAIR, ORAL THESIS DEFENSE

ACCEPTED BY _____ (Signature on File)
DOREEN D. EDWARDS, DEAN
KAZUO INAMORI SCHOOL OF ENGINEERING

ACCEPTED BY _____ (Signature on File)
NANCY J. EVANGELISTA, ASSOCIATE PROVOST
FOR GRADUATE AND PROFESSIONAL PROGRAMS
ALFRED UNIVERSITY

ACKNOWLEDGEMENTS

A scientific theory is a well-substantiated explanation of some aspect of the natural world, based on a body of facts that have been repeatedly confirmed through observation and experiment. Such fact-supported theories are not "guesses" but reliable accounts of the real world. The theory of biological evolution is more than "just a theory." It is as factual an explanation of the universe as the atomic theory of matter or the germ theory of disease. Our understanding of gravity is still a work in progress. But the phenomenon of gravity, like evolution, is an accepted fact.

-American Association for the Advancement of Science, Publisher of the *Journal Science*

First and foremost I would like to extend my deepest gratitude to my advisor, Dr. Carty. His unwavering support provided me with the required motivation for graduate school. Neither could I complete the program without our (usually long) discussions about my work. My knowledge of science and engineering has grown exponentially in the past years because of the advisement I received from Dr. Carty. Thank-you for everything.

Ultimately, Diamond Innovations and Alfred University has paid for my Ph.D. degree. I would like to extend my gratitude. Without the source of funding it would not have been feasible for me to work towards obtaining my degree.

I would like to thank my committee for always having me in the back of their mind and pushing me through the program. Without the help of Dr. Amarakoon, I would not have been able to continue the program. He took me under his wing and personally tutored me for the Ph.D. qualifying examination. Dr. Hall has sent me interesting articles pertaining to my thesis and has had a lot of experience with myself (being on my M.S. committee as well). Dr. Eklund has offered insight into my work which would have been overlooked if not because of his background. I am in great debt to them all and they deserve to be acknowledged for the time and effort they put into my thesis, this work is as much theirs as it is mine.

I can't forget the help Thomas Lam and the rest of the graduate students have given me. In addition to having fellow graduate students to bounce ideas off of and help train me on specific instruments, Gerry Wynick and Swavek have also greatly helped me and have made my life much easier with their insight.

My parents are the ones who planted the seed in my head making me believe that I can do anything if I put my mind to it and work my hardest. Although it took me a while to listen, I

know that without them and their love for me I would not be who I am today. I want you to know that you did an excellent job as parents and I wouldn't change anything in my life, I have no regrets.

My brother, Chad, has been a constant source of procrastination for me, and I want to say thank-you. Without him constantly bringing me back to reality (taking me to baseball games, having me over his apartment to hang out and relax, somehow convincing me to pay \$50 to play fantasy baseball (not to mention getting me to pay to "play" fantasy hockey), and for introducing me to Joey Lilac (still undefeated)) I would have definitely lost my sanity a long time ago (the movies "A Beautiful Mind" and " π " come to mind).

I cannot forget the continued support I receive from my Aunt Maureen and John Hartley. We all have had a lot of fun throughout the years. From camping (that one time) to joyriding around in a corvette, we always had and will have a great time together.

I owe a lot to my Grandma as well. We have so much fun whenever we get together. I will never forget picking those blackberries out in the Hamptons that one day. She has also taught me how to cook. Ever since I was old enough to eat I can remember cooking with her. I will always have and use that skill and she will always be with me in the kitchen.

My friends have also been a continual source of inspiration for me. Joe Pellegrini has been my best friend for the past 11 years. He (and his family) has always been there for me and has supported me. Sean Cunningham has made my life as a T.A. much easier than it should have been (especially this past semester). Eric Liddington has helped me the past couple of years with testing some of my hypotheses experimentally. Kristen Steinhauer has been my friend for the longest period of time; she has seen me through my worst and still continues to talk to me for some unseen reason. She has seen me transform my life from being a kid in high school to being incorporated in a group of people that includes the most brilliant minds in history, without ever trying to tell me to do otherwise.

When it comes down to it, Patty Selock has made me want to become a better person. She has transformed her life for me and has supported all of my decisions for the past 4 years. I am so happy to have found someone that I can relate to so easily. With Patty it is so easy to be myself and I will always love her, no matter what.

The last person I would like to thank is my high school chemistry teacher, Ralph D'Ambrosio. Mr. D'Ambrosio was the person that introduced me to the real world of science and taught me

that learning can be a lot of fun. He is one of the best teachers that I have had and deserves credit for everything that I have done (academically) in my life.

Finally, I would just like to say that this acknowledgement section has probably been the hardest to write for two reasons: 1) I didn't want to forget anybody, and 2) I have not used the words "I", "me", "my", "myself", etc. in writing for the past 9 years. Thank-you Alfred University for giving me a top-class education and thank-you to anyone that I forgot.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
1.0 Van der Waals Attractive Potential.....	3
2.0 Repulsive Potential	16
3.0 Total Interaction Potential	28
4.0 List of Variables	30
5.0 References	34
II. PAPER #1.....	40
1.0 Title.....	40
2.0 Keywords	40
3.0 Abstract	40
4.0 Introduction	40
5.0 Determination of Spectral Parameters	42
6.0 Previous Approach to Approximate non-Retarded Hamaker Constant	44
6.1 Characterization of the Mediums	45
6.2 Characterization of Colloids	52
7.0 Hamaker Constant Calculations	60
8.0 Conclusions	63
9.0 List of Variables	64
10.0 References	65
III. PAPER #2.....	68
1.0 Title.....	68
2.0 Keywords	68
3.0 Abstract	68
4.0 Introduction	68
5.0 Experimental	70
6.0 Results and Discussion.....	73
7.0 Conclusions	84
8.0 List of Variables	85
9.0 References	87

IV. PAPER #3.....	89
1.0 Title.....	89
2.0 Keywords	89
3.0 Abstract	89
4.0 Introduction	89
5.0 Experimental	90
6.0 Results and Discussion.....	93
6.1 Rheology of the Suspensions.....	93
6.2 Determination of Stability Mechanism.....	96
7.0 Conclusions	98
8.0 References	99
V. PAPER #4.....	100
1.0 Title.....	100
2.0 Keywords	100
3.0 Abstract	100
4.0 Introduction	100
5.0 Experimental	101
6.0 Results and Discussion.....	104
6.1 Repulsive Potential	104
6.2 Attractive Potential	107
6.3 Total Interaction Potential	109
7.0 Conclusions	121
8.0 List of Variables	122
9.0 References	123
VI. CONCLUSIONS	126
VII. APPENDIX A: ELLIPTICAL INTEGRAL PROGRAM.....	129
1.0 Program.....	129
2.0 References	131

LIST OF TABLES

	Page
Table I. Non-aqueous Systems Which are Frequently Used in Ceramic Processing	1
Table II. Frequently Used Dispersants in Non-aqueous Processing	2
Table III. Effect of Photon Absorption on the Material at Different Regions of the Electromagnetic Spectrum	7
Table IV. Demonstration That at Room Temperature (298K) the Interval Sampling Frequency is 2.5×10^{14} rad/sec	11
Table V. Dielectric Dispersion Properties of the Suspension Mediums	48
Table VI. Bandgaps of the Colloids Used to Determine the Applicability of the Bandgap Approximation	53
Table VII. Comparison of Non-retarded Hamaker Constants Calculated With and Without the Microwave Relaxation Included	57
Table VIII. Dielectric Dispersion Properties of the Powders Used in this Study	59
Table IX. Comparison of Non-retarded Hamaker Constant (at 298K) in Water with the Ionic Character of the Bond	60
Table X. Non-retarded Hamaker Constants ($\times 10^{-20}$ J) for the Selected Materials in the Various Mediums at 298K	62
Table XI. Suspension Medium Properties	70
Table XII. Characterization of the Powders Used in this Study	71
Table XIII. Calculated Debye-lengths of Particles in the Selected Suspension Mediums Assuming Symmetrical Electrolytes with a Valence of $z=1$	74
Table XIV. ζ -potential Values (mV) for Each Powder in Each Solvent	77

Table XV.	Properties of Each of the Suspending Mediums Used.....	91
Table XVI.	Characterization of the Colloids Used in the Suspensions.....	92
Table XVII.	Specific Viscosity ($\times 10^3$) at a Shear Rate of 1.0s^{-1} for Each Suspension Tested.....	95
Table XVIII.	Characterization of the Suspending Mediums Used.....	102
Table XIX.	Characterization of the Colloids Tested in Order of Increasing Electronegativity Difference.....	104
Table XX.	Corrected ζ -potential Measurements (mV) of the Colloids in the Various Mediums at 298K.....	106
Table XXI.	Calculated Non-retarded Hamaker Constants ($\times 10^{-20}\text{J}$) at 298K Between Similar Colloids in Each Medium	108
Table XXII.	Suspensions Which Were Predicted to be Unstable via Total Interaction Potential Calculations.....	112
Table XXIII.	Determination of the Thermal Boundary (in $\text{J/m}^2 \times 10^{-6}$) of the Suspensions in the Reduced Experimental Matrix	115
Table XXIV.	Shear Thinning Exponents, n , of the Experimental Matrix in Which the Stability was Deemed Unknown. Suspensions Labeled N/A were Deemed Unstable.....	117
Table XXV.	Equilibrium Separation Distance (in nm) at the Secondary Minimum for Suspensions in Which the Stability was Unknown	117
Table XXVI.	Results Using the Flow Chart in Figure 22 to Discern the Stability of the Suspension.....	120
Table A-I.	Add-in Program Used to Calculate First Order Elliptical Integrals.....	129
Table A-II.	Example Table of Solutions to the First Order Elliptical Integral Adapted from Abramowitz ¹	130
Table A-III.	Add-in Program Used to Calculate Second Order Elliptical Integrals	130

Table A-IV. Example Table of Solutions to the Second Order Elliptical Integral Adapted from Abramowitz ¹	130
--	-----

LIST OF FIGURES

	Page
Figure 1. Schematic of the double-layer of a positively charged colloid adapted from Shaw. ⁶⁷	17
Figure 2. Curves used to demonstrate the four possible types of interactions between colloidal particles in a medium.....	29
Figure 3. Schematic of the band structure of solids demonstrating the concept of a bandgap.	42
Figure 4. Schematic diagram demonstrating the physical significance of the dielectric dispersion properties used for calculations	44
Figure 5. Non-retarded Hamaker constant as a function of the refractive index of the medium demonstrating that for some materials there is a correlation between the two.....	51
Figure 6. Correlation of the approximated Hamaker constant with the Hamaker constant using the accepted ω_{UV} value excluding the non-oxide materials	54
Figure 7. Correlation of the approximated Hamaker constant with the Hamaker constant using the accepted ω_{UV} value	55
Figure 8. Comparison of non-retarded Hamaker constants calculated via the Pugh approximation and the bandgap approximation with the published values for oxide materials.....	56
Figure 9. Comparison of total interaction potentials for vitreous silica as a function of separation distance in water.	58
Figure 10. Measured ζ -potential as a function of applied voltage for vitreous silica in all mediums that resulted in a non-zero ζ -potential.	73
Figure 11. Graphical representation of the effect that ion concentration has on the Debye-length.....	75

Figure 12. Electrostatic potential as a function of distance for A-AKP in selected mediums.	79
Figure 13. Effect of two interacting colloids on the (net) electrostatic potential as a function of separation distance for A-AKP in selected mediums.	81
Figure 14. Calculated repulsive potential as a function of separation distance for A-AKP in selected mediums.	83
Figure 15. Specific viscosity as a function of shear rate for vitreous silica in selected mediums.	94
Figure 16. Demonstration that shear thinning exponent and specific viscosity is a function of suspending medium.	97
Figure 17. Isoelectric points of some of the colloidal particles tested adapted from Parks. ³²	103
Figure 18. Repulsive potential generated in vitreous silica as a function of separation distance for different suspending mediums. The static dielectric constant of each medium is noted in the parentheses.	107
Figure 19. Total van der Waals attractive potential as a function of separation distance and calculated non-retarded Hamaker constants ($\times 10^{-20}$ J) for vitreous silica in parentheses next to the identified medium.	109
Figure 20. Total interaction potential curves of vitreous silica as a function of separation distance for the selected mediums.	110
Figure 21. Vitreous silica and anatase suspended in methanol demonstrating the smaller thermal boundary calculated in anatase was overcome by the particles.	116
Figure 22. Flow chart depicting the requirements to discern if a suspension will be stable or not using DLVO theory.	119

ABSTRACT

Application of DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory for suspensions utilizing non-aqueous suspension mediums has been tested. Prediction of suspension stability using DLVO theory requires the calculation of the attractive and repulsive forces between the suspended colloids and that the only significant stabilization mechanism present is electrostatic stabilization which was tested.

The van der Waals attractive potential was calculated for 12 different colloids in 11 suspending mediums in accord with Lifshitz's treatment and a new approximation proposing that the material bandgap energy can be used to approximate the Hamaker constant was developed. This treatment requires the complete knowledge of the permittivity as a function of frequency for all the components in the respective suspension. The permittivity data was simplified using a damped oscillator model described by Ninham and Parsegian. All permittivity data was compiled from the literature. Microwave data was tabulated by NIST, infrared parameters were determined from FTIR data, and the ultraviolet/visual parameters were determined via Cauchy plots or estimated by the bandgap. Using the bandgap to approximate the ultraviolet/visual parameters proved to be more accurate than other approximations when compared to the accepted values. It was found that the non-oxide and non-stoichiometric colloids tested had the largest associated van der Waals attractive force. The van der Waals potential calculated for oxide particles was found to follow a direct relationship with the ionic character of the bonding.

Repulsive forces were calculated for 12 different colloids in 11 suspending mediums. The calculated repulsive potential generated is a function of both the magnitude of charge generated on each colloid (ζ -potential) and the size of the interacting double-layers. ζ -potential was measured for each suspension using a microelectrophoretic technique and the double-layer thickness was calculated. It was demonstrated that as the polarity of the suspending medium increased, the thickness of the double-layer also increased. A large double-layer thickness was found to directly correlate to the suspension stability. A large double-layer thickness results in a decreased slope of the charge degradation from the colloidal surface to the bulk suspension. This coupled with a large magnitude of surface charge increases the probability of dispersion.

Through viscosity measurements, the stability mechanism of each suspension was determined by comparison of the viscosity at a shear rate of 1.0s^{-1} with the shear thinning exponent. It was determined that, of the suspension mediums tested, heptane, octanoic acid, and poly(ethylene

glycol) introduce non-electrostatic stabilization mechanisms significant enough to invalidate the DLVO predictions for suspensions made using those mediums.

Consistent with DLVO theory, the total interaction potential was calculated by summation of the repulsive and attractive potentials of each suspension (84 suspensions total) as a function of separation distance. Based upon the results of the summation, the suspension stability can be predicted. 64 of the 84 suspensions were determined to be unstable as the colloids agglomerated in the primary minimum, 11 suspensions were determined to be weakly flocculated, and nine suspensions were found to be stable. Viscosity was used to determine the critical value for the thermal energy barrier and to test the DLVO predictions. The critical value of the thermal energy barrier was found to be $2.0 \times 10^{-6} \text{J/m}^2$. Therefore, for suspensions calculated to have a thermal energy barrier less than the critical value, the Brownian motion of the colloids in suspension at 298K were enough to overcome it, resulting in agglomeration at the primary minimum. For suspensions with a thermal barrier larger than $2.0 \times 10^{-6} \text{J/m}^2$, the interacting colloids moved into the secondary energy minimum. All suspensions tested in which the thermal energy barrier was less than $2.0 \times 10^{-6} \text{J/m}^2$ had a specific viscosity at a shear rate of 1.0s^{-1} greater than the cut-off viscosity for stability. If the colloids moved into the secondary minimum, the resulting suspension was characterized as either being weakly flocculated or stable. Weakly flocculated suspensions had an equilibrium separation distance of colloids less than 40nm resulting in a viscosity at a shear rate of 1.0s^{-1} larger than the determined specific viscosity cut-off (1.1×10^4), but a shear thinning exponent greater than 1.0. Stable suspensions were defined by the colloids as having an equilibrium separation distance greater than 40nm, resulting in viscosity values at a shear rate of 1.0s^{-1} smaller than that of the determined cut-off viscosity value.

I. INTRODUCTION

Non-aqueous processing of ceramics is not uncommon and is driven by drawbacks associated with processing in water, including the tendency to chemically react with some powders, the inability to dissolve specific (i.e. non-polar) additives, and the relatively low volatility.^{1,2} In many cases, organic mediums are mixed together in order to control the volatility. Extremely fast evaporation may cause a state similar to “case hardening” in spray drying, where a hard shell develops during drying.^{1,3} The mediums, which are mixed, must be miscible and are sometimes azeotropic. It is apparent that the type of mixture (azeotropic or miscible) will affect the suspension and drying properties; however, it is unclear whether the medium mixture affects the final product.^{1,4}

Regardless of this regulation, many non-aqueous suspension systems have proven effective; the most common mediums used include ethanol and 2-butanone (Table I).¹

Table I. Non-aqueous Systems Which are Frequently Used in Ceramic Processing

Medium(s)	Corresponding Powder System	Reference(s)
Ethanol	Al ₂ O ₃ , BaTiO ₃	1-3,5-9
Methanol/Methyl Isobutyl Ketone (MIBK)	Al ₂ O ₃ , Si ₃ N ₄	10-12
2-Butanone (MEK)	Various	1,2,5
Acetone	Various	6-9
MEK/Anhydrous Ethanol	Various	1-3,13-19
MEK/95% Ethanol	Various Titanates	1,13,17,20-22
MEK/Methanol	Various	1
MEK/Methanol/Butanol	Glass-Ceramics	1,23
MEK/Acetone	Al ₂ O ₃ -SiO ₂ -B ₂ O ₃	1,24
MEK/Toluene	Glass-Ceramics	1,5,25
1,1,1 Trichloroethane (TCE)	MgO	1-3
TCE/95% Ethanol	Al ₂ O ₃	1,13,16
Benzene	Various	6,8,9,26,27
Toluene	Various	1,5,7-9,28,29
Toluene/95% Ethanol	Various	1
Toluene/Methanol	BaTiO ₃	4
Xylenes/Anhydrous Ethanol	Al ₂ O ₃	1,30
Butanol/Isopropanol/Xylenes/Nitropropane	Various	1

Although many different industries utilize non-aqueous processing techniques, there is limited understanding of how to predict stability. This lack of knowledge has created a recipe book of trade secrets for each company involved in non-aqueous processing. These recipes often involve the use of additives to induce dispersion. Many dispersants have been proposed and tested for non-aqueous systems (Table II). An agreement on the mechanisms for dispersion has not been reached; though the main particle separation mechanism has been found to be steric hindrance, it is speculated that both steric and electrostatic mechanisms are significant.¹ A global flow chart for predicting dispersion is needed. The first step into understanding the behavior of non-aqueous suspensions is to evaluate the validity of DLVO theory.

Table II. Frequently Used Dispersants in Non-aqueous Processing

Dispersant	Reference(s)
Menhaden Fish Oil	2,29-31
Phosphate Esters	11,14-18,22,31,32
Ethoxylates	17
Triglycerides	29
Dibutyl Amine	5
Glycerol Trioleate	31
Benzene Sulfonic Acid	31

This work hypothesizes that dispersant additions are not required for most non-aqueous suspensions. Through understanding the interactions of the colloids in the suspension a medium may be selected which will induce dispersion without the need for additives. It is the goal of this work to develop a method to predict suspension stability in different mediums and to demonstrate that dispersion can be accomplished simply through proper selection of the medium.

DLVO theory is the most robust model developed to predict dispersion. This theory was first developed in 1941 by Derjaguin and Landau and in 1948 Verwey and Overbeek independently arrived at the same result.^{33,34} DLVO theory models the interactions between electrical double-layers (the electrostatic effects) using a force balance approach. This approach does not apply when other dispersion mechanisms, such as electrosteric or steric (where particles are physically restrained from interaction), are significant. DLVO theory is expressed by the competition between two forces, the van der Waals attractive force and a repulsive force formed due to

surface interactions of the colloid with the medium, from which a total interaction potential between colloids can be calculated by the summation of the repulsive and attractive forces over the separation distance. The theory has been proven to be valid for aqueous suspensions; however, similar results were not obtained for suspensions using non-aqueous mediums. Since deviation from DLVO theory occurs when using non-aqueous mediums to suspend colloids, it has been proposed that other “non-DLVO” forces exist.^{35,36} It is hypothesized that these “non-DLVO” forces reported are due to inclusion of another stabilization mechanism and does not warrant the conclusion that DLVO theory is invalid for non-aqueous mediums. It is hypothesized (and the basis for this study) that the DLVO theory can be applied successfully to non-aqueous suspensions and can therefore be used to predict mediums which will induce dispersion without the use of additives.

Application of DLVO theory requires the calculation of the total interaction potential between suspended colloids. Calculation of the van der Waals attractive potential was done in accord with the Lifshitz theory and the repulsive force was calculated using the Gouy-Chapman model. The total interaction potential (calculated from the summation of the van der Waals attractive potential and the repulsive potential) was used to predict the suspension stability. Viscosity measurements were used in the study for two reasons: 1) test the dispersion predictions and 2) confirm that an electrostatic stabilization mechanism was the only significant mechanism acting within a suspension.

1.0 Van der Waals Attractive Potential

The intrinsic van der Waals forces associated with the colloidal particles originate due to the dipolar nature of the solids and the interaction of the respective dipoles with one another.³⁷ There are three different forces which contribute to the total van der Waals force. The first is described by Keesom as an orientation effect.^{37,38} The Keesom force originates from interacting permanent dipoles and the effect that their relative orientations have on interaction energy. Attraction and repulsion can both be obtained from dipole interactions; therefore, if all orientations were equally realized, the net force between atoms/molecules would be zero. However, Boltzmann statistics suggests that orientations of lower energy are statistically preferred; the most favorable (lowest energy) orientation for atoms/molecules is one that results in the net force being negative which corresponds to an attractive force (all variables are defined at the end of the chapter):

$$U_{Keesom} = -\frac{2}{3K_B T} \frac{\mu_1^2 \mu_2^2}{D^6} \quad (1)$$

From Equation 1 it is observed that the energy of attraction between the atoms/molecules is indirectly proportional to the separation distance – as the separation between the atoms/molecules increases, the Keesom force will decrease on the order of D^6 . For low temperatures or short separation distances Equation 1 is not valid because the atoms/molecules cannot have a more energetically favorable position than parallel to each other, therefore:

$$U_{Keesom} = -\frac{2\mu_1\mu_2}{D^3} \text{ for } \frac{\mu_1\mu_2}{D^3} \gg K_B T \quad (2)$$

Equation 2 only describes the orientation effects on the attraction between the atoms/molecules for a parallel orientation, whereas Equation 1 incorporates all possible orientations.

The Keesom force has a strong correlation to temperature due to the manifestation of Boltzmann statistics in the calculations; therefore, as temperature increases the net Keesom force decreases. However, Debye observed that as temperature increases the van der Waals force does not decrease as rapidly as Keesom predicted.^{37,38} Debye hypothesized that an interaction energy independent of temperature existed between particles. In addition to the orientation effects, interacting atomic/molecular dipoles will also affect the distribution of charge within atoms/molecules, called the induction effect. The property to induce a change in charge distribution in surrounding molecules is described by the polarizability. U_{Debye} is the magnitude of the interaction potential due to the induction effect:

$$U_{Debye} = -\frac{1}{D^6} (\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2) \quad (3)$$

Much like the attractive potential obtained from Keesom, Debye also showed an indirect relationship between interaction potential and D on the order of D^6 . The Debye force, generated

from the induced charge distributions, resolved the problem with temperature dependence (U_{Debye} is not a function of temperature); however, it did not explain how perfectly symmetrical atoms/molecules with no permanent dipoles (gases such as He, H₂, N₂, and CH₄) exhibit van der Waals forces.

Debye hypothesized the existence of quadrupole moments in the atoms/molecules, which also contribute to the induction of dipoles through interaction of these higher-order moments. Though this does occur, the effect is negligible and it can be shown through wave mechanics that symmetrical gases do not exhibit any multipole. Although wave mechanics proved Debye's hypothesis pertaining to development of van der Waals forces in perfectly symmetrical gases to be false, wave mechanics also provided the solution. Transient dipoles are produced within the symmetrical gases and other non-polar molecules since (according to wave mechanics) the electrons are always in motion. The instantaneous dipole moments produce an electric field within the atom/molecule which then acts upon a neighboring atom/molecule, producing an induced dipole and subsequent electric field with a magnitude based upon the polarizability. The induced electric field is in phase with the original (the induced dipoles are in phase with the transient dipoles producing them). The zero-point electron motion is augmented when absorption of photons from (background) radiation takes place. The absorption of photons perturbs the electronic orbitals and produces a transient dipole moment different from those produced at the zero-point motion. These dipole moments formed from excitation of the atom/molecule have the same effect on neighboring atoms/molecules as the transient dipole moments formed from the zero-point motion. The dispersion force produced was first described by London.³⁷

$$U_{London} = -\frac{3}{2} \frac{\alpha_1 \alpha_2}{D^6} \frac{\Phi_1 \Phi_2}{\Phi_1 + \Phi_2} = -\frac{\lambda}{D^6} \quad (4)$$

London's theory assumed that each atom/molecule responds instantaneously to the electric field produced by the neighboring atoms/molecules due to the formation of transient dipoles.^{37,39} However, the produced electric field travels at the speed of light and the electrons travel at a speed consistent with the frequency of the characteristic radiation which is absorbed and emitted from the respective atom/molecule. Therefore if the separation distance between the two atoms/molecules is larger than the wavelength of the characteristic radiation, the charge

distribution in the atom/molecule originally producing the electric field will have changed in the time it takes for the electric field to travel from the original atom/molecule to the neighboring atoms/molecules. This phase lag effect is known as retardation and is accompanied by the fact that as the separation distance between the atoms/molecules in question increases past the wavelength of the absorbed characteristic radiation, the van der Waals attractive force decreases:^{39,40}

$$U_{London}(D \rightarrow \infty) = -\frac{23}{8\pi^2} \frac{hc}{D^7} \alpha_1 \alpha_2 \quad (5)$$

Equation 5 demonstrates that as the separation distance increases past the characteristic wavelength, the attractive potential decreases more rapidly (proportional to D^{-7} rather than D^{-6}) due to the phase lag. As long as the two atoms/molecules in question are relatively close (separation distance $< 20\text{nm}$) the van der Waals forces will be non-retarded.

The van der Waals forces were applied to colloids by Hamaker by combining the separate contributing forces (Keesom, Debye, and non-retarded London potentials) into a single equation, by a pair-wise summation method, and then separating the geometrical and material specific terms (Equation 6).⁴¹ Through this treatment, Hamaker presented what is now known as the Hamaker constant, A , which incorporates all the material specific variables and scales directly with the van der Waals attractive force:

$$V_A = -A \frac{1}{12\pi D^2} \quad (6)$$

The Hamaker constant involves all of the material specific terms and the other terms in Equation 6 describe the geometry of the system. The Hamaker constant was calculated from the polarizabilities and atomic densities through a pair-wise summation in the two interacting bodies.⁴¹

$$A = \pi^2 q^2 \lambda \quad (7)$$

Hamaker's pair-wise summation approach, referred to as the microscopic approach, had shortcomings in calculating the attractive potential, including neglecting many body interactions, not being able to calculate for the effect of a different suspending medium (rather than vacuum), and not accounting for retardation effects.^{3,39,42}

These limitations were corrected by Lifshitz. Although Lifshitz arrived at the same expression for total van der Waals potential between particles (Equation 6), the calculation of the Hamaker constant is much different.⁴² Lifshitz hypothesized that each colloid can be modeled as a dielectric continuum. Due to instantaneous dipole formation and subsequent electric field generation, each body can therefore be thought of as a series of standing waves which occur at specific frequencies based on the polarization of the atom/molecule at different frequencies.⁴³ Most materials are able to be polarized in several different ways leading to a combined effect of the Debye and London forces (the Keesom force does not describe polarization, it describes the effect of orientation of dipoles on the net force). The contribution of each can be observed by the dielectric frequency response which is material specific. Table III shows the result of the absorption of photons at different frequencies of the electromagnetic spectrum.

Table III. Effect of Photon Absorption on the Material at Different Regions of the Electromagnetic Spectrum

Electromagnetic Region	Frequency (rad/sec) ⁴⁴		Photon Absorption Effect ⁴⁵	Polarization Type
	Low	High		
Radio	10^4	10^{10}	Plasma oscillation	N/A
Microwave	10^9	10^{12}	Molecule/atom rotation	Orientational
Infrared	10^{12}	3×10^{15}	Molecular vibration	Molecular
Visible	3×10^{15}	5×10^{15}	Molecular electronic excitation	Molecular/Electronic
Ultraviolet	5×10^{15}	10^{18}	Valence shell electron excitation	Electronic
X-ray	10^{17}	10^{21}	Core shell electron excitation	N/A
Gamma Ray	10^{19}	10^{23}	Nuclear excitation	N/A

For metals or electronic conductors, photons corresponding to the radio wave frequencies of the electromagnetic spectrum are absorbed. For other materials, however the photon energy is too weak to be absorbed except under special conditions when specific nuclei are placed under a strong magnetic field (NMR).⁴⁵ Relaxations in the microwave region correspond to rotational movement of molecules and will only occur if there is a change in the dipole moment during the rotation and therefore can only affect molecules with a permanent dipole moment. The rotation corresponds to orientation polarization (Keesom/Debye forces) effect. In the infrared range, absorption of photons will cause molecular bonds to vibrate. This absorption can only occur if the excitation of the molecule causes a change in the magnitude and direction of the dipole moment of the bond (Debye force).⁴⁵ There are two specific vibrational classifications – stretching and bending. The ultraviolet/visible regions cause changes in the electronic state of the molecule/atom in which electrons are excited to higher energy orbitals (in atoms) and/or anti-bonding levels (in molecules). These changes induce atomic and molecular electronic polarization (Dispersion/Debye force). At frequencies larger than those in the ultraviolet range (X-rays and γ -rays), the response of the polarization processes (orientational, molecular, and electronic) to the field does not occur. Therefore, at these frequencies the permittivity of the material approaches the permittivity of free space (ϵ_0) and is not taken into account when calculating van der Waals forces.

The resulting van der Waals force can then be calculated as a result of modifications in the electromagnetic field between two bodies to cause the interacting fields to be in phase. Therefore, the role of the suspending medium is to modify the interacting electromagnetic field between colloidal particles. Furthermore, the Hamaker constant must be calculated with knowledge of the dielectric spectra (of each component) as a function of frequency. Since the van der Waals force is a function of separation distance between interacting particles (retardation effect), the Hamaker constant is not a constant but also function of separation distance, which has been defined by Lifshitz:^{42,46,47}

$$A_{132}(D, T) = \frac{3K_B T}{2} \sum'_{n=0} \beta_n^2 \int_1^\infty \rho \{ \ln[1 - \Delta_n \exp(-\rho \beta_n)] + \ln[1 - \Delta \exp(-\rho \beta_n)] \} d\rho \quad (8)$$

Where the prime on the summation indicates that the first term ($n=0$) is taken at half weight; ρ , β_n , Δ_n , and Δ can be defined as:

$$\rho = \sqrt{\frac{\omega^2}{c^2} - q^2} \quad (9)$$

$$\beta_n = \frac{2\xi_n D}{c} \sqrt{\varepsilon_3(i\xi_n)} \quad (10)$$

$$\Delta_n = \frac{\left(s_1 - \rho \varepsilon_1(i\xi_n) / \varepsilon_3(i\xi_n) \right) \left(s_2 - \rho \varepsilon_2(i\xi_n) / \varepsilon_3(i\xi_n) \right)}{\left(s_1 + \rho \varepsilon_1(i\xi_n) / \varepsilon_3(i\xi_n) \right) \left(s_2 + \rho \varepsilon_2(i\xi_n) / \varepsilon_3(i\xi_n) \right)} \quad (11)$$

$$\Delta = \frac{(s_1 - \rho)(s_2 - \rho)}{(s_1 + \rho)(s_2 + \rho)} \quad (12)$$

The variable q is defined via the Fourier integral of the random electrical field vector, $\mathbf{E}$. The function $\mathbf{E}(x, y, z)$ is represented by a two dimensional planar vector, $\mathbf{q}$, and a radius vector, $\mathbf{r}$, in the y-z plane of the Fourier integral. Therefore $\mathbf{q}$ has components k_y and k_z resulting in $k^2 = k_x^2 + q^2$ and the quantity of q includes values from zero to infinity. The component s_j (where $j = 1$ or 2) is defined as:

$$s_j = \sqrt{\frac{\varepsilon_j(i\xi_n)}{\varepsilon_3(i\xi_n)} - 1 + \rho^2} \quad (13)$$

The permittivity is a complex function, $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ of a complex frequency $\omega = \omega_R + i\xi$ defined by:

$$\varepsilon(\omega + i\xi) = 1 + \int_0^\infty f(\tau) \exp(i\omega\tau) \exp(-\xi\tau) d\tau \quad (14)$$

The function $\varepsilon(i\xi_n)$ arises from a purely mathematical evaluation of the permittivity on an imaginary frequency axis and has no direct physical significance:

$$\varepsilon(i\xi) = 1 + \int_0^{\infty} f(\tau) \exp(-\xi\tau) d\tau \quad (15)$$

Equation 15 is derived from extending the definition of the permittivity (dielectric response; Equation 14) of a material to the complex frequencies. Therefore, it can be determined from Equation 15 that when $\xi = 0$, $\varepsilon(i\xi_n)$ is equal to the static dielectric constant and at $\xi = \infty$, $\varepsilon(i\xi_n)$ is equal to unity. The imaginary frequency axis is used in order to change the path of integration when calculating the van der Waals force in order to simplify the mathematics.⁴²

The physical significance of $\varepsilon(i\xi_n)$ can only be inferred indirectly by relation to the physical quantities of the real (transmission) and imaginary (absorption) permittivity through Kramers-Kronig transformations. From these relationships it is observed that the values of permittivity on the imaginary frequency axis are a function of dispersion energy. The complex permittivity on the imaginary frequency axis, $\varepsilon(i\xi_n)$, is determined by relation to the imaginary component of permittivity on the real frequency axis, $\varepsilon''(\omega)$, which measures the ability of a material to absorb an electric field at specific frequencies (known as the Kramers-Kronig transformation).⁴⁷

$$\varepsilon(i\xi_n) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega \varepsilon''(\omega)}{\omega^2 + \xi_n^2} d\omega \quad (16)$$

Since $\varepsilon''(\omega) > 0$, $\varepsilon(i\xi_n)$ is a real, positive, and monotonically decreasing function of ξ_n ($n = 0, 1, 2, 3, \dots$) where:

$$\xi_n = \frac{4\pi^2 K_B T}{h} n \quad (17)$$

Equation 17 demonstrates that the permittivity of a material is only measured at specific frequencies, a consequence of evaluation on an imaginary axis. Therefore by calculating the frequencies at which permittivity is evaluated, it is concluded that the ultraviolet region is the most important (Table IV).

Table IV. Demonstration That at Room Temperature (298K) the Interval Sampling Frequency is 2.5×10^{14} rad/sec

Electromagnetic Region	Frequency (rad/sec) ⁴⁴		Number of Samples (at 298K)
	Low	High	
Static	-	-	1
Radio	10^4	10^{10}	0
Microwave	10^9	10^{12}	0
Infrared	10^{12}	3×10^{15}	12
Visible	3×10^{15}	5×10^{15}	8
Ultraviolet	5×10^{15}	10^{18}	4057

For simplicity, the Hamaker function is reduced to a constant (with respect to separation distance) for two specific cases: when the van der Waals force is either fully non-retarded ($D \ll$ characteristic wavelength) or fully retarded ($D \rightarrow \infty$). For a non-retarded van der Waals force between two different particles, the Hamaker function can now be defined as the Hamaker constant:^{42,48,49}

$$A_{132} = \frac{3K_B T}{2} \sum_{n=0}^{\infty} \int_0^{\infty} \sigma \ln[1 - \Delta_{13} \Delta_{23} \exp(-\sigma)] d\sigma \quad (18)$$

The Δ_{jk} and σ terms are defined as:

$$\Delta_{jk} = \frac{\varepsilon_j(i\xi_n) - \varepsilon_k(i\xi_n)}{\varepsilon_j(i\xi_n) + \varepsilon_k(i\xi_n)} \quad (19)$$

$$\sigma = \frac{2\rho\xi_n D}{c} \sqrt{\varepsilon_3(i\xi_n)} \quad (20)$$

$\varepsilon_j(i\xi_n)$ and $\varepsilon_k(i\xi_n)$ are the permittivity of component j ($j=1, 2$, or 3) and component k ($j=1, 2$, or 3) where $k \neq j$. Since $\Delta_{13}\Delta_{23} \exp(-\sigma) < 1$, the integral in Equation 18 can be preformed analytically by expanding the logarithmic term in a power series and integrating term by term:

$$A_{132} = \frac{3K_B T}{2} \sum_{n=0}^{\infty} \sum_{\nu=1}^{\infty} \frac{(\Delta_{13}\Delta_{23})^{\nu}}{\nu^3} \quad (21)$$

When only one type of particle is used, Equation 21 can be reduced to:

$$A_{131} = \frac{3K_B T}{2} \sum_{n=0}^{\infty} \sum_{\nu=1}^{\infty} \frac{(\Delta_{13})^{2\nu}}{\nu^3} \quad (22)$$

For fully retarded values of the van der Waals force, the Hamaker function (Equation 8) is reduced to:

$$A_{132} = \frac{hc\pi}{480} \frac{1}{\sqrt{\varepsilon_{r,static,3}}} \left(\frac{\varepsilon_{r,static,1} - \varepsilon_{r,static,3}}{\varepsilon_{r,static,1} + \varepsilon_{r,static,3}} \right) \left(\frac{\varepsilon_{r,static,2} - \varepsilon_{r,static,3}}{\varepsilon_{r,static,2} + \varepsilon_{r,static,3}} \right) \Omega(\varepsilon_{r,static,1}, \varepsilon_{r,static,2}, \varepsilon_{r,static,3}) \quad (23)$$

The Lifshitz retardation function has a range of values from 0.35 ($\sigma \rightarrow 1$) to unity ($\sigma \rightarrow \infty$).

All calculations for Hamaker function and non-retarded Hamaker constant require the permittivity as a function of imaginary frequency, $\varepsilon(i\xi_n)$, of each component to be known. In order to obtain this information, knowledge of the entire complex permittivity on a real frequency axis from zero to infinity is required and then used to calculate $\varepsilon(i\xi_n)$ via Equation 16. The information required is not readily available for many materials; however, by treating the permittivity as damped oscillators, the required information can be reduced.⁴⁶ This treatment, developed by Ninham and Parsegian, models the complex permittivity using a Debye relaxation

for the microwave region and a Lorentz electron dispersion term for infrared through ultraviolet wavelengths.⁴⁶

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = 1 + \frac{C_{mw}}{1 - \left(\frac{i\omega}{\omega_{mw}}\right)} + \sum_j \frac{C_j}{1 - \left(\frac{\omega}{\omega_j}\right)^2 + i\gamma_j\omega} \quad (24)$$

On the imaginary axis, $\omega = i\xi_n$:

$$\varepsilon(i\xi_n) = 1 + \frac{C_{mw}}{1 + \left(\frac{\xi_n}{\omega_{mw}}\right)} + \sum_j \frac{C_j}{1 + \left(\frac{\xi_n}{\omega_j}\right)^2 - \gamma_j\xi_n} \quad (25)$$

Contribution of the damping term is now only significant when $\omega \approx \omega_j$ since the bandwidths will always be less than the absorption frequencies. Therefore the damping term is negligible since:

$$1 + \left(\frac{\xi_n}{\omega_j}\right)^2 \gg \gamma_j\xi_n \quad (26)$$

Resulting in:

$$\varepsilon(i\xi_n) = 1 + \frac{C_{mw}}{1 + \left(\frac{\xi_n}{\omega_{mw}}\right)} + \sum_j \frac{C_j}{1 + \left(\frac{\xi_n}{\omega_j}\right)^2} \quad (27)$$

The microwave and infrared terms are well documented or can be inferred through FTIR spectroscopy.⁵⁰⁻⁵³ The data for frequencies in the visible/ultraviolet range of the spectrum is not as easily obtainable. A common method of discerning the spectroscopic data in this region is to

use the first ionization potential as the characteristic absorption frequency in the ultraviolet/visible region, ω_{UV} . As long as the absorption within the visible region is negligible, the characteristic oscillator strength, C_{UV} , in this region can be calculated by correlation to the refractive index at the sodium D line (wavelength = 589.29nm):

$$C_{UV} = n_s^2 - 1 \quad (28)$$

The sodium D line is the most common wavelength at which the refractive index is measured. Therefore Equation 28 correctly assumes that after the ultraviolet relaxation, the relative permittivity of the material is unity and no polarization mechanisms can activate. A more precise way to determine these relaxations is to correlate refractive index data to the Ninham-Parsegian representation of the dielectric dispersion. In the ultraviolet region for only real frequencies:

$$\varepsilon(\omega) = 1 + \int_0^{\infty} f(\tau) \exp(i\omega\tau) d\tau \cong 1 + \frac{C_{UV}}{1 + \left(\frac{\omega}{\omega_{UV}}\right)^2} \quad (29)$$

Since permittivity, $\varepsilon(\omega)$, is a complex material property, the real (ε') component is related to the transmission of the electric field and the imaginary (ε'') component is determined by the materials absorption of the electric field:

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \quad (30)$$

When no absorption of interacting electromagnetic radiation is occurring, $\varepsilon''(\omega) = 0$ (as is observed in the visible frequencies for dielectrics); the permittivity as a function of real frequency can be related to the refractive index as a function of real frequency. The refractive index is a measure of the change in velocity of the interacting light when moving from one medium to another and is closely related to permittivity. Similar to permittivity, refractive index

is a complex material property in which the real part, $n'(\omega)$, is related to the transmission of the interacting light and the complex part, $n''(\omega)$, is related to the absorption of interacting light:

$$n(\omega) = n'(\omega) + in''(\omega) \quad (31)$$

In the region where $\varepsilon''(\omega) = 0$, $n''(\omega)$ is also equal to 0: By applying a Kramers-Kronig transformation, the relationship between $\varepsilon(\omega)$ and $n(\omega)$ when $\varepsilon''(\omega) = 0$ and therefore $n''(\omega) = 0$ can be written as:

$$\varepsilon(\omega) = \varepsilon'(\omega) = n^2(\omega) = 1 + \frac{C_{UV}}{1 - \left(\omega/\omega_{UV}\right)^2} \quad (32)$$

Therefore, rearranging Equation 32:

$$n'(\omega)^2 - 1 = \left(n'(\omega)^2 - 1\right) \frac{\omega^2}{\omega_{UV}^2} + C_{UV} \quad (33)$$

A plot of $n'(\omega)^2 - 1$ vs. $\omega^2(n'(\omega)^2 - 1)$ will yield a straight line with the slope equal to $1/\omega_{UV}^2$ and a y-intercept equal to C_{UV} . Using the first ionization potential data (instead of the Cauchy plot method), values of ω_{UV} are systematically low while values for the oscillator strength, C_{UV} , are slightly high. Using the Cauchy method is therefore preferred, however when the refractive index data is unavailable the first ionization potential can be used.

Hamaker constant and subsequent attractive force calculations have been completed for many different colloidal particles in water. These calculations are enabled by the extensive dielectric dispersion data for water; however, the required dispersion data are not available for other liquids.^{38,54,55} Due to the lack of dispersion data for non-aqueous mediums, calculations of Hamaker constants for colloids suspended in non-aqueous media are typically approximated.^{38,41,42,48,56,57} New characterization techniques have recently been applied to non-

aqueous mediums generating the required dielectric dispersion properties.⁵⁸ This has permitted accurate Hamaker constant calculations.

2.0 Repulsive Potential

The charged double-layer developed by particles when introduced to a medium is the basis for the electrostatic repulsive potential. Similar to the behavior in water, colloids develop a surface charge in organic fluids (regardless of polarity) and therefore also develop a double-layer due to association of free ions in solution.^{6,7,16,59-65} The double-layer consists of two distinct layers of ions which are found in solution in the suspension, known as the Stern layer and the Gouy-Chapman layer (or diffuse layer) which are separated by the shear plane. The Stern layer is located adjacent to the particle surface and consists of adsorped (strongly held) ions which are essentially immobile. The Gouy-Chapman layer is located past the shear plane (towards the bulk suspension) and consists of weakly bound ions allowing for movement.³ The shear plane is named as such because it marks the region where the suspending medium is first able to move with respect to the particle.⁶⁶ The ζ -potential is a measure of the charge at the shear plane. A schematic of the double-layer is presented in Figure 1.

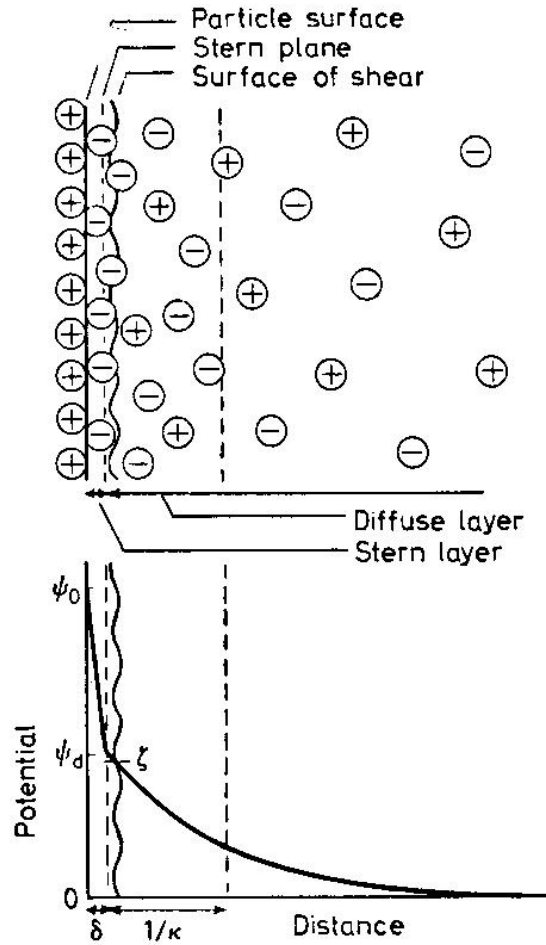


Figure 1. Schematic of the double-layer of a positively charged colloid adapted from Shaw.⁶⁷

Development of the surface charge and subsequent generation of the double-layer in water (and other highly polar media, relative static permittivity, $\epsilon_r > 25$) has been well studied and understood. Charge is developed through ionization of the colloidal surface, resulting in the exchange of protons between the medium and the colloid.⁶⁵ This surface ionization results in the release of hydronium and hydroxyl (as well as other metal/non-metal) ions into solution in which they are complexated (commonly referred to as solvation). Ions in solution must be complexated (acquire a layer of tightly bound molecules) in order to overcome the coulombic forces, $E_{Coulombic}$, of attraction between them (Equation 34).

$$E_{Coulombic} = \frac{-e^2}{4\pi\epsilon_r\epsilon_o D} \quad (34)$$

If the ions were permitted to reach separation distances in which the kinematic energy (Brownian motion) could not overcome the coulombic attraction, the solution would spontaneously precipitate. For example, the separation distance required for a NaCl-water solution at room temperature to spontaneously coalesce is 0.7nm. Therefore in order to prevent ions from entering separation distances which cause spontaneous precipitation (i.e. $\leq 0.7\text{nm}$ for NaCl) the ions must be complexated.⁶⁰

Development of surface charges in low polarity mediums is not as well understood – based on the difficulty to reach dispersion it is hypothesized that ions may not be ionized from the particle surface or the ions do not reach the degree of complexation required to prevent spontaneous coalescence and therefore do not form a sufficiently charged double-layer. For salt solutions in hydrocarbons (non-polar mediums), the critical separation distance is calculated to be approximately 28nm; therefore, a solvation layer of 14nm is required for each ion. Charge on the particle surface and a subsequent double-layer, however has been observed in non-polar mediums with no added electrolyte.^{60,62,64}

It is proposed that a different mechanism is responsible for particle charging in non-aqueous mediums since the degree of dissociation of non-polar suspensions is much less than that of a polar medium.⁶⁰ Fowkes proposed the most robust model for charging in non-aqueous media through a study of added polyelectrolytes (specifically long-chain sulfonic acids) in non-polar mediums.⁶⁸ In water (and other polar mediums), polyelectrolytes first dissociate and then preferentially adsorb onto the particle surface. In non-aqueous media the mechanism was observed to be much different – the polyelectrolyte is not dissociated first but adsorbed on the colloidal surface. Once adsorbed, the polyelectrolyte dissociates by proton exchange. The dissociated polyelectrolyte then undergoes a dynamic process of adsorption-desorption. It is hypothesized that this theory may be applied to non-polar suspension mediums, such as heptane, and long chain polymer suspension mediums, such as poly(ethylene glycol), with no added electrolyte necessary to explain the measured charge on the particle.

Repulsive forces develop in accordance to the overlap of the two interacting double-layers. When two similar particles (particles which develop the same charge in the respective medium) interact, a repulsive force is developed based on electrostatics (like charges repel). Particles

become electrostatically dispersed when the repulsive charges are large enough to overcome the intrinsic van der Waals attractive force between particles. Polar mediums allow for larger ionic double-layers to develop due mainly to the associated relative static permittivity of the medium. The large relative static permittivity of polar media allow for ions at relatively large distances away from the particle surface to be incorporated into the ionic double-layer. Ions are not as easily associated at large distances away from the particle surface in non-polar mediums. This leads to a large charge gradient in non-polar mediums – the charge quickly decays as one moves from the particle surface to the bulk suspension requiring the particles to be closer together before the double-layers interact, resulting in the van der Waals attractive force between particles to also be increased (van der Waals force is proportional to (D^{-6})).^{62,63} Therefore the requirements for electrostatic stability are not only a significant charge on the particle (measured as the ζ -potential), but also a shallow charge gradient (small decay of charge from the shear plane towards the bulk suspension).

Although the charge gradient and size of the double-layer are important, ζ -potential has been commonly used as the benchmark to predict dispersion. It is a common misconception that a large measured ζ -potential will result in dispersion. This has even led to an ASTM standard (now defunct) that defines the minimum ζ -potential needed for dispersion.⁶⁹ Although ζ -potential is related to dispersion, it is often seen, especially in non-polar mediums, that large ζ -potential values can be observed without dispersion.

The ζ -potential is important however, since it is used to calculate a number of suspension properties including diffuse layer (volume) charge density, diffuse double-layer electrostatic potential, diffuse double-layer interaction potential, and the interaction potential energy of repulsion.

The diffuse layer charge density is a measure of excess counter-ions within the double-layer relative to the number of co-ions. This can be calculated by first using the Boltzmann equation to determine the number of ions of each type within the Gouy-Chapman layer and then adding all the ions in a unit volume of the electrolytic solution in the locality of the particle. The Boltzmann equation (Equation 35) relates the number of ions of type i in the double-layer to the number of ions of the same type in the bulk:

$$n_i = n_i^o \exp\left(\frac{-w_i}{K_B T}\right) \quad (35)$$

It is assumed that w_i can be calculated by the electrostatic energy the double-layer acquires:

$$w_i = z_i e \psi \quad (36)$$

The value of the electrostatic potential within the bulk is taken as zero ($\psi = 0$ in the bulk). Therefore to calculate the diffuse layer charge density, all the ions (of either sign) must be added:

$$\rho = \sum_i n_i z_i e = \sum_i n_i^o z_i e \exp\left(\frac{-w_i}{K_B T}\right) \quad (37)$$

From the diffuse layer charge density, the potential throughout the double-layer may be calculated. The diffuse double-layer electrostatic potential is a fundamental quantity necessary for assessment of particle dispersions. Given the theory of electrostatics, a relation between the diffuse double-layer electrostatic potential and the volume charge density is given by the Poisson differential equation:⁶⁶

$$\frac{d^2 \psi}{dx^2} = \frac{-\rho}{\epsilon_{r,static} \epsilon_o} \quad (38)$$

This results in the Poisson-Boltzmann second-order nonlinear differential equation for determination of the diffuse double-layer electrostatic potential within the Gouy-Chapman layer about the particle:

$$\frac{d^2 \psi}{dx^2} = \frac{-1}{\epsilon_{r,static} \epsilon_o} \sum_i n_i^o z_i e \exp\left(\frac{-z_i e \psi}{K_B T}\right) \quad (39)$$

This differential equation can be linearly approximated (called the Debye-Hückel approximation) if it is assumed that the diffuse double-layer electrostatic potential is small relative to the thermal energy of the ions; that is to say that $|z_i e \psi| < K_B T$. Therefore, the exponential can be expanded and all but the first two terms neglected resulting in the difference in the volume charge density of the ions in the bulk (first term within the parentheses, Equation 40) and the ions interacting with the particle (second term within the parentheses, Equation 40):

$$\frac{d^2 \psi}{dx^2} = \frac{-1}{\epsilon_{r,static} \epsilon_o} \left(\sum_i n_i^o z_i e - \sum_i \frac{n_i^o z_i^2 e^2 \psi}{K_B T} \right) \quad (40)$$

The volume charge density of the bulk solution must equal zero to preserve electroneutrality, resulting in:

$$\frac{d^2 \psi}{dx^2} = \frac{\left(\sum_i n_i^o z_i^2 e^2 \right) \psi}{\epsilon_{r,static} \epsilon_o K_B T} = \kappa^2 \psi \quad (41)$$

From Equation 41 the Debye-length can be defined as a measure of the double-layer thickness. The Debye-length is a function of the suspension medium and the type of electrolytes present therefore, the double-layer thickness does not depend on the type of particle in suspension. The Debye-length is the inverse of Equation 42 (κ^{-1}):

$$\kappa = \sqrt{\frac{e^2}{\epsilon_{r,static} \epsilon_o K_B T} \sum_i 1000 M_i N_A z_i^2} \quad (42)$$

Solving the differential equation (Equation 41) results in the Debye-Hückel approximation of the diffuse double-layer electrostatic potential:

$$\psi = \zeta \exp[-\kappa(x-d)] \quad (43)$$

The term $x - d$ defines the distance from the shear plane. The Debye-Hückel approximation is applicable only when the charge on the shear plane is less than 50mV. Above such potentials the linear approximation does not decrease as quickly as the potential actually does when moving from the shear plane towards the bulk resulting in overestimations of the electrostatic potential.⁶⁶ The Debye-Hückel approximation is commonly applied to ceramic systems since ζ -potential values are not generally observed above 50mV; however, when working with non-aqueous suspensions ζ -potential values greater than 100mV without any electrolyte additions have been observed. Therefore, the diffuse double-layer electrostatic potential cannot be modeled by the linear approximation in non-aqueous systems and the full solution to Equation 39 is required.

To simplify the algebra the electrolyte is assumed to be symmetrical ($z_+:z_-$) resulting in $z_i=z_+=-z_- =z$. Therefore we can rewrite Equation 39:

$$\frac{d^2\psi}{dx^2} = \frac{2n^0ze}{\epsilon_{r,static}\epsilon_o} \sinh\left(\frac{ze\psi}{K_BT}\right) \quad (44)$$

Equation 44 is the fundamental differential equation. For this case, the linear approximation yields the Debye-Hückel parameter when only symmetrical electrolytes are present in solution, κ_s :

$$\frac{d^2\psi}{dx^2} = \frac{2n^0z^2e^2}{\epsilon_{r,static}\epsilon_oK_BT} \psi = \kappa_s^2\psi \quad (45)$$

The fundamental differential equation (Equation 44) can be solved:

$$\tanh\left(\frac{ze\psi}{4K_BT}\right) = \tanh\left(\frac{ze\zeta}{4K_BT}\right) \exp[-\kappa_s(x-d)] \quad (46)$$

Equation 46 represents the full solution to the Poisson-Boltzmann differential equation with only symmetrical electrolytes present; however, the electrostatic potential term is not isolated. It is common to study colloidal suspensions using a reduced potential term, ψ_R , which is a dimensionless quantity equal to $e\psi/K_B T$. Although this is how colloidal suspensions are studied, it would be more direct (and tangible) to solve Equation 46 for ψ . It can be shown that by using the area hyperbolic tangent function (artanh), the diffuse double-layer electrostatic potential can be solved for analytically:

$$\psi = \frac{4K_B T}{ze} \operatorname{artanh} \left[\tanh \left(\frac{ze\zeta}{4K_B T} \right) \exp[-\kappa(x-d)] \right] \quad (47)$$

Equation 47 allows for graphical representation of ψ versus D . Knowledge of the diffuse double-layer electrostatic potential allows for the calculation of the diffuse double-layer interaction potential. When double-layers of interacting particles overlap, a significant increase in the electrostatic potential results. At large separation distances (distances close to that of the Debye-length) the cumulative electrostatic potential is simply additive; however, when the separation distance between particles decreases, the cumulative electrostatic potential is more complex. This is because the shape of the diffuse double-layer interaction potential curve is limited by the Poisson-Boltzmann equation (Equation 39) and the fundamental differential equation (Equation 44). To simplify the mathematics, Equation 44 can be reduced to:

$$\frac{d^2 y}{d\xi^2} = \sinh(y) \quad (48)$$

To solve Equation 48 for the electrostatic potential at any point between two interacting particles, the following boundary conditions must be satisfied, at the mid-point plane (where $x = m$):

$$y = u = \frac{ze\psi_m}{K_B T} \quad (49)$$

$$\frac{dy}{d\xi} = 0 \quad (50)$$

Therefore a solution can be found:

$$\frac{dy}{d\xi} = -\sqrt{2 \cosh(y) - 2 \cosh(u)} \quad (51)$$

To calculate the electrical potential function, Equation 51 must be integrated between the limits $x = d$ and $x = m$ (or $y = b$ and $y = u$). The result is an elliptical integral of the first kind:

$$\int_z^u \frac{dy}{\sqrt{\cosh(y) - \cosh(u)}} = -\int_0^{\kappa m} d\xi = -\kappa_s m \quad (52)$$

Elliptical integrals cannot be determined analytically but tabulated solutions have been published.⁷⁰ An elliptical integral of the first kind has the general formula of:

$$F(\phi, k) = \int_0^\phi \frac{d\theta}{\sqrt{1 - k^2 \sin^2(\theta)}} \quad (53)$$

Therefore solving for the total separation distance, D , Equation 52 can be transformed to fit the general formula of an elliptical integral:

$$D = 4\kappa_s^{-1} \exp(k) \left[F\left(\frac{\pi}{2}, k\right) - F(\phi, k) \right] \quad (54)$$

where k and ϕ are defined respectively:

$$k = \exp(-u) \quad (55)$$

$$\phi = \cos^{-1} \left[\exp \left(\frac{(\psi_m - \zeta)ze}{2K_B T} \right) \right] \quad (56)$$

From Equation 54, the electrostatic potential at the mid-point plane can be calculated as a function of particle separation distance.

The repulsive potential generated from the electrostatic potential between the two interacting particles is analyzed by calculation of osmotic pressure developed because of the accumulation of ions between particles:

$$p = cRT = nK_B T \quad (57)$$

The osmotic pressure is related to the repulsive potential by the difference between the osmotic pressure at the mid-point between the interacting particles and the osmotic pressure in the bulk suspension.

$$V_R = - \int_{\infty}^D \Delta p dD \quad (58)$$

With respect to the osmotic pressure, the fundamental differential equation (Equation 44) can be integrated for a fixed separation distance:

$$2n^o ze \cosh(y) - \frac{\epsilon_{r,static} \epsilon_o}{2} \left(\frac{d\psi}{dx} \right)^2 = C \quad (59)$$

The first term in Equation 59 is related to the osmotic pressure between the particles, and the second term is known as the Maxwell stress. The pressure varies from point to point due to the variation of local ion concentration resulting in the variability of ψ . At the mid-point plane between the two particles, $d\psi/dx$ is equal to zero resulting in the osmotic pressure being equal to C . Therefore, the osmotic pressure at the mid-point plane between the two interacting particles is:

$$p_m = C = 2n^o z e \cosh(u) \quad (60)$$

Through the identity of the hyperbolic cosine, Equation 60, can be reduced to:

$$p_m = K_B T (n_+ + n_-)_m \quad (61)$$

Equation 61 demonstrates that as the distance increases away from the mid-point plane toward the particle surface, the number of ions will increase. It could be thought that the increase in ions will result in increasing the osmotic pressure associated with the plane (one between the particle surface and the mid-point plane) however, this is not the case since the Maxwell stress (second term in Equation 59) will cause the net effect to be the same throughout the entire region between plates.

As stated, the force per unit area exerted on the particles is calculated as the difference between the osmotic pressure between the solution and the mid-point plane between the interacting particles. This results in the solution:

$$\Delta p = K_B T (n_+ + n_- - 2n^o) = 2n^o K_B T [\cosh(u) - 1] \quad (62)$$

Therefore an expression for the osmotic pressure difference can be defined using known variables. To calculate the repulsive potential, however the integral of Δp with respect to the interparticle separation distance must be considered. This leads to an elliptical integral of the

second kind (integral of the elliptical integral used to calculate ψ_m). An elliptical integral of the second kind has the form:

$$E(\phi, k) = \int_0^{\phi} \sqrt{1 - k^2 \sin^2(\theta)} d\theta \quad (63)$$

A program was developed to return the tabulated results of both the first and second order elliptical integrals as a function of ϕ and k (Appendix A).

In order to simplify the mathematics involved, the repulsive potential can be determined by relating the osmotic pressure difference to the difference in free energy. This results in:

$$V_R = 2(U_m - U_{\infty}) \quad (64)$$

U_m is then the only term with a second order elliptical integral in which:

$$U_m = -2n^o K_B T \kappa_s^{-1} \left[\frac{D}{4\kappa_s^{-1}} (3\exp(u) - 2 - \exp(-u)) + 2\sqrt{2\cosh(b) - 2\cosh(u)} + I \right] \quad (65)$$

The second order elliptical integral, I , (Equation 65) is equivalent to:

$$I = 2 \int_u^b \frac{\exp(-y) - \exp(u)}{\sqrt{2\cosh(y) - 2\cosh(u)}} dy \quad (66)$$

Solutions to Equation 66 can be solved by using Equation 63 and therefore must be reduced to:

$$I = -2 \exp\left(\frac{u}{2}\right) \left[E\left(\frac{\pi}{2}, \exp(-u)\right) - E\left(\sin^{-1}\left[\exp\left(-\frac{b-u}{2}\right)\right], \exp(-u)\right) \right] \quad (67)$$

By substituting Equation 67 into Equation 65, U_m can be determined. U_∞ can be found by restricting Equation 65 to the case of $m=\infty$ which results in the explicit expression:

$$U_\infty = -2n^\circ K_B T \kappa_s^{-1} \left[4 \cosh\left(\frac{b}{2}\right) - 4 \right] \quad (68)$$

With both U_m and U_∞ able to be solved, the total repulsive potential between two interacting particles can now be calculated by substituting Equations 68 and 65 into Equation 64.

3.0 Total Interaction Potential

The total interaction potential is realized by the summation of the attractive and repulsive terms (V_A and V_R) as a function of separation distance:

$$V_T = \sum_{D=2nm}^{20nm} \left[-A_{132} \frac{1}{12\pi D^2} + 2(U_m - U_\infty) \right] \quad (69)$$

Since the non-retarded Hamaker constant is being used, the summation is only valid from 2 to 20nm where the retardation effects are negligible.

By determining the total potential energy between two colloids as a function of separation distance (Figure 2), it can be determined if the colloids will exhibit a repulsive or attractive nature and at what distance the colloids will be from one another when energetically stabilized. Therefore the stability of the suspension can be determined.

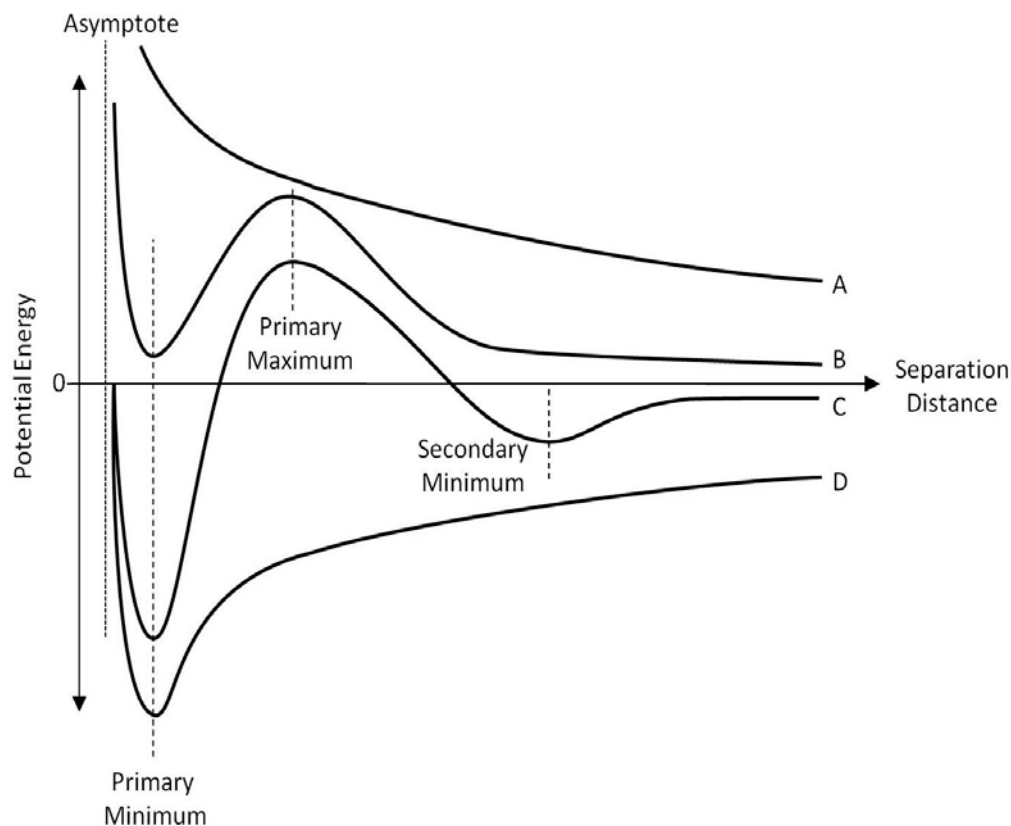


Figure 2. Curves used to demonstrate the four possible types of interactions between colloidal particles in a medium. The curves depicted are exaggerated to illustrate the features of each.

Figure 2 depicts four distinct curves for the total interaction potential between colloids. Curve A is a demonstration of the effect of a large repulsive potential coupled with a weak attractive potential. No minimum value is apparent leading to the prediction of a stable colloidal suspension. Curve A is represented by a positive primary maximum potential and no primary or secondary minimum potentials. Curve B also demonstrates a large repulsive potential, however, it is coupled with a larger attractive potential than in curve A. Therefore Curve B is represented by a positive primary maximum and primary minimum potential with no existing secondary potential. The larger attractive potential results in a primary maximum and minimum. Although a minimum is present, the colloidal particles must be given enough energy to overcome the energy barrier at the primary maximum. Typically in this case, the energy barrier is much greater than the thermal energy associated with the colloids and therefore the separation between colloids is never reduced enough for the colloids to reside at the primary minimum. Therefore

the effect is the same as curve A and a suspension with a total interaction potential described by curve B is predicted to be stable. Curve C demonstrates the coupling of a moderate repulsive and attractive potential with one another. As in curve type B, a primary minimum and maximum is developed; however, unlike curve B a secondary minimum is observed in curve C. The predicted stability of the colloidal suspension in curve C is dependent on two variables – the magnitude of the energy barrier (difference between the primary maximum and the secondary minimum) and the separation distance associated with the secondary minimum. If the magnitude of the energy barrier is smaller than the thermal energy associated with the colloids, the colloids will overcome the maximum and therefore reside at the primary minimum resulting in irreversible coagulation and therefore predicted instability. However, if the colloids do not possess the required energy to overcome the barrier they will reside at the secondary minimum. The secondary minimum results in weakly attractive particles at relative large equilibrium separation distances. In the secondary minimum stability of the suspension is hypothesized to be dependent on the equilibrium separation distance – it is speculated that large distances between particles (even though they are weakly attractive) will result in a stable suspension. In curve D, the attractive potential is much larger than the repulsive potential and is defined by a negative primary minimum potential with no primary maximum or secondary minimum. Suspensions with the interaction potential described by curve D will result in the particles residing at the primary minimum; therefore, an unstable suspension is predicted by DLVO theory.

4.0 List of Variables

A – Hamaker constant

A_{131} – Hamaker constant between colloids of material type 1 separated by a dielectric medium (3)

A_{132} – Hamaker constant between two different colloids of material type 1 and 2 separated by a dielectric medium (3)

A_j – Hamaker constant of material j in the Pugh approximation

$$b - \frac{ze\zeta}{K_B T}$$

c – Speed of light in a vacuum

C_{mw} – Characteristic oscillator strength of the microwave frequency range

C_{IR} – Characteristic oscillator strength of the infrared frequency range
 C_{UV} – Characteristic oscillator strength of the ultraviolet frequency range
 C_j – Characteristic oscillator strength of the infrared or ultraviolet frequency range
 D – Total separation distance
 d – Distance from the particle surface to the shear plane
 $E_{Coulombic}$ – Electrostatic Coulombic force between ions
 e – Charge on an electron
 h – Planck's constant
 I – Second order elliptical integral
 K_B – Boltzmann's constant
 M_i – Molarity of ion i
 m – Distance from the particle surface to the mid-point plane
 N_A – Avogadro's number
 n – Integer
 n_i – Number of ion of type i in the double-layer
 n_+ – Number of positive ions in the double-layer
 n_- – Number of negative ions in the double-layer
 n_i^o – Number of ion of type i in the bulk suspension per unit volume
 $n(\omega)$ – Index of refraction as a function of real frequency
 $n'(\omega)$ – Real component of refractive index (transmission)
 $n''(\omega)$ – Imaginary component of refractive index (absorption)
 n_s – Real refractive index at the sodium D line
 p – Osmotic pressure
 q – Atomic density
 R – Gas constant

T – Temperature

U_{Keesom} – Average interaction potential between atoms/molecules due to the Keesom force

U_{Debye} – Interaction potential due to the induction effect

U_{London} – Interaction potential due to the London dispersion effect

U_m – Free energy at the mid-point plane between interacting particles

U_∞ – Free energy of the bulk suspension

$$u - \frac{ze\psi_m}{K_B T}$$

V_R – Total repulsive potential

V_A – Total van der Waals attractive potential

V_T – Total interaction potential

w_i – Work required to move an ion of type i from the bulk suspension to the double-layer

x – Distance from the particle surface

$$y - \frac{ze\psi}{K_B T}$$

z_i – Valence of ion i

α_j – Polarizability of atom/molecule j

Δ_{ij} – Difference in dielectric dispersion between materials i and j

$\epsilon_{r,static}$ – Relative static permittivity (Dielectric constant)

ϵ_0 – Permittivity of a vacuum

ϵ_r – Relative permittivity

$\epsilon(\omega)$ – Complex permittivity as a function of real frequency

$\epsilon'(\omega)$ – Real permittivity as a function of real frequency (transmission)

$\epsilon''(\omega)$ – Imaginary permittivity as a function of real frequency (absorption)

$\epsilon_j(i\xi_n)$ – Permittivity of material j evaluated on the imaginary frequency axis ($i\xi_n$)

ξ_n – Imaginary frequency

$f(\tau)$ – Function which describes the decay of the induced polarization with time

γ_j – Damping term

Φ_j – First ionization energy of atom/molecule j

κ^{-1} – Debye-length

κ_s^{-1} – Debye-length only including symmetrical electrolytes

λ - London-van der Waals constant

η – Viscosity at 298K

$\Omega(\epsilon_{r,static,1}, \epsilon_{r,static,2}, \epsilon_{r,static,3})$ – Lifshitz retardation function for material type 1 and 2 separated by a dielectric medium (3)

τ – Time

μ_j – Dipole moment of atom/molecule j

ν – Integer

ω – Real frequency

ω_{mw} – Characteristic frequency of the microwave frequency range

ω_R – Characteristic frequency of the infrared frequency range

ω_{UV} – Characteristic frequency of the ultraviolet frequency range

ω_j – Characteristic frequency of the infrared or ultraviolet frequency range

ψ – Electrostatic potential

ψ_r – Reduced potential

ψ_m – Electrostatic potential at the mid-point plane

ζ – ζ -potential

5.0 References

1. R.E. Mistler and E.R. Twiname, *Tape Casting: Theory and Practice*; p. 298. American Ceramic Society, Westerville, OH, 2000.
2. R.E. Mistler, D.J. Shanefield, and R.B. Runk, "Tape Casting of Ceramics," pp. 411-48 in *Ceramic Processing before Firing*. Edited by G. Y. Onoda and L. L. Hench. John Wiley & Sons, New York, 1978.
3. M.N. Rahaman, *Ceramic Processing and Sintering*, 2nd ed.; p. 875. Marcel Dekker, New York, 2003.
4. S. Bhattacharjee, M.K. Paria, and H.S. Maiti, "Polyvinyl Butyral as a Dispersant for Barium Titanate in a Non-Aqueous Suspension," *J. Mater. Sci.*, **28** [23] 6490-5 (1993).
5. J.-C. Lin, T.-S. Yeh, C.-L. Cherng, and C.-M. Wang, "The Effects of Solvents and Binders on the Properties of Tape Casting Slurries and Green Tapes," pp. 197-204 in *Ceramic Transactions, Vol. 26, Forming Science and Technology*. Edited by M. J. Cima. American Ceramic Society, Westerville, OH, 1992.
6. J.M. Thwala, J.W. Goodwin, and P.D. Mills, "Electrokinetic Studies of Colloidal Silica Particles Dispersed in Non-Aqueous Media in the Presence of a Nonionic Surfactant, Dodecylhexaethylene Glycol Monoether ($C_{12}E_6$)," *Colloids Surf., A*, **335** [1-3] 33-42 (2009).
7. U. Paik, V.A. Hackley, S.-C. Choi, and Y.-G. Jung, "The Effect of Electrostatic Repulsive Forces on the Stability of $BaTiO_3$ Particles Suspended in Non-Aqueous Media," *Colloids Surf., A*, **135** [1-3] 77-88 (1998).
8. Y. Chen, Y. Liang, F. Zheng, R. Zhou, and Z. Feng, "Dispersion Behavior of Si-C-N Nanopowders in Organic Liquids," *Ceram. Int.*, **27** [1] 73-9 (2001).
9. Y. Hirata and M. Kawabata, "Dispersion and Consolidation of Ultrafine Barium Titanate ($BaTiO_3$) Powder in Non-Aqueous Solutions," *Mater. Lett.*, **16** [4] 175-80 (1993).
10. M.D. Sacks and G.W. Scheiffele, "Polymer Adsorption and Particulate Dispersion in Nonaqueous Al_2O_3 Suspensions Containing Poly(Vinyl Butyral) Resins," pp. 175-84 in *Advances in Ceramics, Vol. 19, Multilayer Ceramic Devices*. Edited by J. B. Blum and W. R. Cannon. American Ceramic Society, Columbus, OH, 1986.
11. C.A. Gutiérrez and R. Moreno, "Tape Casting of Non-Aqueous Silicon Nitride Slips," *J. Eur. Ceram. Soc.*, **20** [10] 1527-37 (2000).
12. M.D. Sacks and C.S. Khadilkar, "Milling and Suspension Behavior of Al_2O_3 in Methanol and Methyl Isobutyl Ketone," *J. Am. Ceram. Soc.*, **66** [7] 488-94 (1983).

13. J.S. Reed, *Principles of Ceramics Processing*; p. 658. John Wiley & Sons, New York, 1995.
14. T. Chartier, E. Streicher, and P. Boch, "Phosphate Esters as Dispersants for the Tape Casting of Alumina," *Am. Ceram. Soc. Bull.*, **66** [11] 1653-5 (1987).
15. K.R. Mikeska and W.R. Cannon, "Non-Aqueous Dispersion Properties of Pure Barium Titanate for Tape Casting," *Colloids Surf.*, **29** [3] 305-21 (1988).
16. F. Boschini, A. Rulmont, R. Cloots, and R. Moreno, "Rheological Behaviour of BaZrO₃ Suspensions in Non-Aqueous Media," *Ceram. Int.*, **35** [3] 1007-13 (2009).
17. K. Mikeska and W.R. Cannon, "Dispersants for Tape Casting Pure Barium Titanate," pp. 164-83 in *Advances in Ceramics, Vol. 9, Forming of Ceramics*. American Ceramic Society, Columbus, OH, 1984.
18. L. Braun, J.R. Morris Jr, and W.R. Cannon, "Viscosity of Tape-Casting Slips," *Am. Ceram. Soc. Bull.*, **64** [5] 727-9 (1985).
19. W.R. Cannon, J.R. Morris, and K.R. Mikeska, "Dispersants for Non-Aqueous Tape Casting," pp. 161-75 in *Advances in Ceramics, Vol. 19, Multilayer Ceramic Devices*. Edited by J. B. Blum and W. R. Cannon. American Ceramic Society, Columbus, OH, 1986.
20. R.J. MacKinnon and J.B. Blum, "Ultrasonic Dispersion of BaTiO₃ Tape Casting Slurries," pp. 158-63 in *Advances in Ceramics, Vol. 9, Forming of Ceramics*. American Ceramic Society, Columbus, OH, 1984.
21. R.J. MacKinnon and J.B. Blum, "Particle Size Distribution Effects on Tape Casting Barium Titanate," pp. 150-7 in *Advances in Ceramics, Vol. 9, Forming of Ceramics*. Edited by J. A. Mangels and G. L. Messing. American Ceramic Society, Westerville, OH, 1984.
22. T. Chartier, E. Jorge, and P. Boch, "Dispersion Properties of BaTiO₃ Tape-Casting Slurries," *J. Eur. Ceram. Soc.*, **11** [5] 387-93 (1993).
23. N. Kamehara, K. Kurihara, and K. Niwa, "Method for Producing Multilayered Glass-Ceramic Structure with Copper-Based Conductors Therein," U.S. Pat. 4,504,339, March 1985.
24. Y. Imanaka, H. Ogawa, M. Tsukada, E. Udagawa, K. Kurihara, H. Yokoyama, and N. Kamehara, "Process for Producing Multilayer Ceramic Circuit Board with Copper," U.S. Pat. 4,679,320, July 1987.

25. J.A. Lewis, K.A. Blackman, A.L. Ogden, J.A. Payne, and L.F. Francis, "Rheological Property and Stress Development During Drying of Tape-Cast Ceramic Layers," *J. Am. Ceram. Soc.*, **79** [12] 3225-34 (1996).
26. J.L. van der Minne and P.H.J. Hermanie, "Electrophoresis Measurements in Benzene-Correlation with Stability I. Development of Method," *J. Colloid Sci.*, **7**, 600-15 (1952).
27. J.L. van der Minne and P.H.J. Hermanie, "Electrophoresis Measurements in Benzene-Correlation with Stability II. Results of Electrophoresis, Stability, and Adsorption," *J. Colloid Sci.*, **8**, 38-52 (1952).
28. J.L. Park, "Manufacture of Ceramics," U.S. Pat. 2,966,719, June 1954.
29. P.D. Calvert, E.S. Tormey, and R.L. Pober, "Fish Oil and Triglycerides as Dispersants for Alumina," *Am. Ceram. Soc. Bull.*, **65** [4] 669-72 (1986).
30. E.M. Anderson, R.A. Marra, and R.E. Mistler, "Tape Casting Reactive Aluminas," *Am. Ceram. Soc. Bull.*, **76** [7] 45-50 (1997).
31. W.R. Cannon, R. Becker, and K.R. Mikeska, "Interactions among Organic Additives Used for Tape casting," pp. 525-41 in *Advances in Ceramics*, Vol. 26, *Ceramic Substrates and Packages for Electronic Applications*. Edited by M. F. Yan. American Ceramic Society, Westerville, OH, 1989.
32. R.M. Cannon, W.H. Rhodes, and A.H. Heuer, "Plastic Deformation of Fine-Grained Alumina (Al_2O_3): I, Interface-Controlled Diffusional Creep," *J. Am. Ceram. Soc.*, **63** [1-2] 46-53 (1980).
33. B. Derjaguin and L. Landau, "Theory of the Stability of Strongly Charged Lyophobic Sols and of the Adhesion of Strongly Charged Particles in Solutions of Electrolytes," *Acta Physicochim. URSS*, **14**, 633-62 (1941).
34. E.J.W. Verwey and J.T.G. Overbeek, *Theory of the Stability of Lyophobic Colloids*; p. 205. Elsevier, New York, 1948.
35. F.J. Rubio-Hernandez, "Is DLVO Theory Valid for Non-Aqueous Suspensions?" *J. Non-Equilib. Thermodyn.*, **24** [1] 75-9 (1999).
36. B.W. Ninham, "On Progress in Forces since the DLVO Theory," *Adv. Colloid Interface Sci.*, **83** [1-3] 1-17 (1999).
37. F. London, "The General Theory of Molecular Forces," *Trans. Faraday Soc.*, **33**, 8-26 (1937).
38. L. Bergstrom, "Hamaker Constants of Inorganic Materials," *Adv. Colloid Interface Sci.*, **70**, 125-69 (1997).

39. D. Tabor and R.H.S. Winterton, "Direct Measurement of Normal and Retarded van der Waals Forces," *Proc. R. Soc. London, A*, **312** [1511] 435-50 (1969).
40. H.B.G. Casimir and D. Polder, "The Influence of Retardation on the London-van der Waals Forces," *Phys. Rev.*, **73** [4] 360 (1948).
41. H.C. Hamaker, "The London-van der Waals Attraction between Spherical Particles," *Physica*, **4**, 1058-72 (1937).
42. E.M. Lifshitz, "The Theory of Molecular Attraction Forces between Solid Bodies," *Sov. Phys. JETP*, **2**, 73-83 (1956).
43. L.D. Landau, L.P. Pitaevskii, and E.M. Lifshitz, *Electrodynamics of Continuous Media*, 2nd ed., Vol. 8; p. 460. Edited by L. D. Landau and E. M. Lifshitz. Butterworth-Heinemann, Oxford, England, 1984.
44. R.A. Serway and R.J. Beichner, *Physics: For Scientists and Engineers with Modern Physics*, 5th ed. Saunders College Publishing, Philadelphia, 2000.
45. R.L. Pecsok, L.D. Shields, T. Cairns, and I.G. McWilliam, *Modern Methods of Chemical Analysis*, 2nd ed.; p. 573. John Wiley & Sons, New York, 1976.
46. B.W. Ninham and V.A. Parsegian, "van der Waals Forces: Special Characteristics in Lipid-Water Systems and a General Method of Calculation Based on the Lifshitz Theory," *Biophys. J.*, **10** [7] 646-63 (1970).
47. I.E. Dzyaloshinskii, E.M. Lifshitz, and L.P. Pitaevskii, "The General Theory of van der Waals Forces," *Adv. Phys.*, **10** [38] 165 - 209 (1961).
48. D.C. Prieve and W.B. Russel, "Simplified Predictions of Hamaker Constants from Lifshitz Theory," *J. Colloid Interface Sci.*, **125** [1] 1-13 (1988).
49. J.N. Israelachvili, "The Calculation of van der Waals Dispersion Forces between Macroscopic Bodies," *Proc. R. Soc. London, A*, **331** [1584] 39-55 (1972).
50. F. Buckley and A.A. Maryott, "Tables of Dielectric Dispersion Data for Pure Liquids and Dilute Solutions," National Bureau of Standards Circular 589 (U.S.), 1958.
51. F.F. Bentley, L.D. Smithson, and A.L. Rozek, *Infrared Spectra and Characteristic Frequencies (700-300cm⁻¹) Collection of Spectra, Interpretation, and Bibliography*; p. 457. Interscience Publishers, New York, 1968.
52. R.A. Nyquist and R.O. Kagel, *Infrared Spectra of Inorganic Compounds (3800-45cm⁻¹)*, Vol. 4; p. 500. Academic Press, New York, 1971.

53. C.J. Pouchert, *The Aldrich Library of Infrared Spectra*, 3rd ed. Aldrich Chemical, Milwaukee, WI, 1981.
54. R.M. Pashley, "The van der Waals Interaction for Liquid Water: A Comparison of the Oscillator Model Approximation and Use of the Kramers-Kronig Equation with Full Spectral Data," *J. Colloid Interface Sci.*, **62** [2] 344-7 (1977).
55. C.M. Roth and A.M. Lenhoff, "Improved Parametric Representation of Water Dielectric Data for Lifshitz Theory Calculations," *J. Colloid Interface Sci.*, **179** [2] 637-9 (1996).
56. B.W. Ninham and V.A. Parsegian, "van der Waals Forces across Triple-Layer Films," *Chem. Phys.*, **52** [9] 4578-87 (1970).
57. L.R. White, R.R. Dagastine, P.M. Jones, and Y.-T. Hsia, "van der Waals Force Calculation between Laminated Media, Pertinent to the Magnetic Storage Head-Disk Interface," *J. Appl. Phys.*, **97** [10] 104503-7 (2005).
58. T. Masuda, Y. Matsuki, and T. Shimoda, "Spectral Parameters and Hamaker Constants of Silicon Hydride Compounds and Organic Solvents," *J. Colloid Interface Sci.*, **340** [2] 298-305 (2009).
59. A. Kitahara, "Stability of Dispersions in Polar Media," *Adv. Colloid Interface Sci.*, **38**, 1-11 (1992).
60. I.D. Morrison, "Electrical Charges in Nonaqueous Media," *Colloids Surf., A*, **71** [1] 1- (1993).
61. W. Wang, S. Martin-Moe, C. Pan, L. Musza, and Y.J. Wang, "Stabilization of a Polypeptide in Non-Aqueous Solvents," *Int. J. Pharm.*, **351** [1-2] 1-7 (2008).
62. R.J. Pugh, "Dispersion and Stability of Ceramic Powders in Liquids," pp. 127-92 in Surfactant Science Series, Vol. 51, *Surface and Colloid Chemistry in Advanced Ceramics Processing*. Edited by R. J. Pugh and L. Bergstrom. Marcel Dekker, New York, 1994.
63. P.C. van der Hoeven and J. Lyklema, "Electrostatic Stabilization in Non-Aqueous Media," *Adv. Colloid Interface Sci.*, **42**, 205-77 (1992).
64. R. Xu, C. Wu, and H. Xu, "Particle Size and Zeta Potential of Carbon Black in Liquid Media," *Carbon*, **45** [14] 2806-9 (2007).
65. R.O. James, "Characterization of Colloids in Aqueous Systems," pp. 349-410 in Advances in Ceramics, Vol. 21, *Ceramic Powder Science*. Edited by G. L. Messing, J. W. McCauley, and K. S. Mazdidasni. American Ceramic Society, Westerville, OH, 1987.
66. R.J. Hunter, *Introduction to Modern Colloid Science*; p. 338. Oxford University Press, New York, 1993.

67. D.J. Shaw, *Introduction to Colloid and Surface Chemistry*, 3rd ed.; p. 273. Butterworth, Boston, 1980.
68. F.M. Fowkes, "Dispersions of Ceramic Powders in Organic Media," pp. 411-21 in *Advances in Ceramics*, Vol. 21, *Ceramic Powder Science*. Edited by G. L. Messing, J. W. McCauley, and K. S. Mazdizyasni. American Ceramic Society, Westerville, OH, 1987.
69. "Zeta Potential of Colloids in Water and Waste Water" ASTM Designation D 4187-82. American Society for Testing Materials, West Conshohocken, PA.
70. United States National Bureau of Standards, Applied Mathematics Series, Vol. 55, *Handbook of Mathematical Functions: With Formulas, Graphs, and Mathematical Tables*; p. 1046. Edited by M. Abramowitz and I.A. Stegun. United States Government Print Office, Washington D.C., 1964.

II. PAPER #1

1.0 Title

The Potential to use the Bandgap Energy of a Material to Approximate Hamaker Constants

Keith J. DeCarlo

William M. Carty

2.0 Keywords

Hamaker Constant, van der Waals potential, Colloids, Non-aqueous medium, Bandgap

3.0 Abstract

The bandgap is a material property that expresses the type of bonding, electrical properties, and optical properties. Bandgap measurements are straightforward and are commonly measured for most materials. It is hypothesized that the bandgap can be used to approximate non-retarded Hamaker constants. Using the bandgap to calculate the non-retarded Hamaker constants presents a unique opportunity to be able to apply DLVO theory to materials, such as semiconductors, in which the characterization of dielectric dispersion in the ultraviolet/visible frequencies range proved difficult. This work demonstrates that using the energy of the bandgap for particles to approximate the characteristic frequency in the ultraviolet/visible frequency range to calculate non-retarded Hamaker constants for oxides correlated well with the published values. Using the bandgap to approximate the non-retarded Hamaker constants for non-oxide materials resulted in significantly underestimated values which require a mathematical correction.

4.0 Introduction

DLVO theory requires the attractive potential between interacting colloids to be known. The contribution of the attractive potential (V_A) was derived by Hamaker (variables are defined at the end of the chapter):¹

$$V_A = -A \frac{1}{12\pi D^2} \quad (70)$$

The Hamaker constant (A) involves all of the material specific terms; the other terms in Equation 70 describe the geometry of the system.

The Hamaker constant is calculated by modeling each colloid as a dielectric continuum. Due to instantaneous dipole formation and subsequent electric field generation, each body can therefore be visualized as a series of standing waves which occur at specific frequencies based on the polarization of the atom/molecule at different frequencies.²

The resulting van der Waals force is calculated through a correlation of the modifications in the electromagnetic field between two bodies causing the interacting fields to be in phase. The role of the suspending medium is to further modify the interacting electromagnetic field between colloidal particles. Furthermore, the Hamaker constant must be calculated with knowledge of the dielectric spectra of each component as a function of frequency, therefore requiring the particles and the suspending medium to be characterized in the microwave, infrared, and ultraviolet/visible frequency regions of the electromagnetic spectrum.

Hamaker constant and subsequent attractive force calculations have been completed for several different colloidal particles in water. These calculations are enabled by the extensive dielectric dispersion data for water; however, the required dispersion data is not always available for other liquids.³⁻⁵ Due to the lack of dielectric dispersion data for most materials, calculations of Hamaker constants for colloids suspended in non-aqueous media are typically approximated.^{1,3,6-9} It is hypothesized that using the bandgap energy to approximate the characteristic frequency and absorption in the ultraviolet/visible frequency range results in a Hamaker constant which is comparable to the value obtained when using the Cauchy method. A bandgap exists in all non-metallic materials and is defined as the energy gap between the valence and conduction band (Figure 3).¹⁰

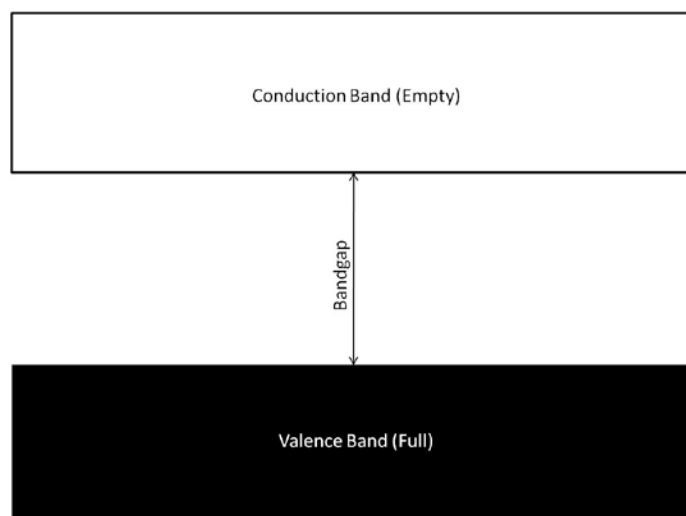


Figure 3. Schematic of the band structure of solids demonstrating the concept of a bandgap.

The energy of the bandgap is defined by the amount of energy required for an electron in the valence band to move into the conduction band.¹⁰⁻¹² Therefore the material will absorb light corresponding to that energy resulting in a dielectric relaxation. Semiconducting materials all absorb in the visible range (bandgap energy $< 2\text{eV}$), making Cauchy analysis on these materials difficult. Bandgap measurements are straightforward and the values are already known for most materials making the bandgap energy a viable candidate to approximate the characteristic absorption frequency and strength when the data and/or analysis instruments for construction of a Cauchy plot is unavailable.

5.0 Determination of Spectral Parameters

Non-retarded Hamaker constants were calculated for an experimental matrix of 132 (12 powder types x 11 mediums) colloid-medium combinations. The suspension mediums used in the calculations included water and 10 other mediums: methanol, ethanol, isopropanol, sec-butanol, acetone, 2-butanone (Methyl Ethyl Ketone), toluene, heptane, octanoic acid, and 200 molecular weight poly(ethylene glycol). 2-Butanone and poly(ethylene glycol) will be identified respectively as MEK and PEG.

Hamaker constants for each colloid/medium suspension combination were calculated using the Lifshitz equation with the Ninham-Parsegian dielectric dispersion oscillator model.^{3,8,13}

$$A_{131} = \frac{3K_B T}{2} \sum_{n=0}^{\infty} \sum_{\nu=1}^{\infty} \frac{(\Delta_{13})^{2\nu}}{\nu^3} \quad (71)$$

Where Δ_{13} is defined as:

$$\Delta_{13} = \frac{\varepsilon_1(i\xi_n) - \varepsilon_3(i\xi_n)}{\varepsilon_1(i\xi_n) + \varepsilon_3(i\xi_n)} \quad (72)$$

All calculations for the Hamaker function and non-retarded Hamaker constant require the permittivity as a function of imaginary frequency, $\varepsilon(i\xi_n)$, of each component to be known. In order to obtain this information, knowledge of the entire complex permittivity on a real frequency axis from zero to infinity is required and then used to calculate $\varepsilon(i\xi_n)$ via Kramers-Kronig relationships.⁴ The information required is not readily available for many materials but by treating the permittivity as damped oscillators, the characteristic absorption frequencies and strengths can be deduced.¹³ This treatment, developed by Ninham and Parsegian, models the complex permittivity using a Debye relaxation for the microwave region and a Lorentz electron dispersion term for infrared through ultraviolet regions.¹³

$$\varepsilon(i\xi_n) = 1 + \frac{C_{mw}}{1 + \left(\frac{\xi_n}{\omega_{mw}}\right)^2} + \sum_j \frac{C_j}{1 + \left(\frac{\xi_n}{\omega_j}\right)^2} \quad (73)$$

The dielectric dispersion parameters for each colloid and medium were characterized within the microwave, infrared, visible, and ultraviolet ranges of the electromagnetic spectrum for use in the Ninham-Parsegian model (Table V). At higher frequencies than ultraviolet, the interacting radiation will not result in the activation of a polarization mechanism, but will cause ionization and ejection of subatomic particles. Therefore at frequencies higher than that of the final ultraviolet relaxation, the relative static permittivity is equal to unity. The spectroscopic dispersion parameters used for water were extracted from Bergström.³ A schematic was prepared to help facilitate the understanding of the dispersion properties required for analysis (Figure 4).

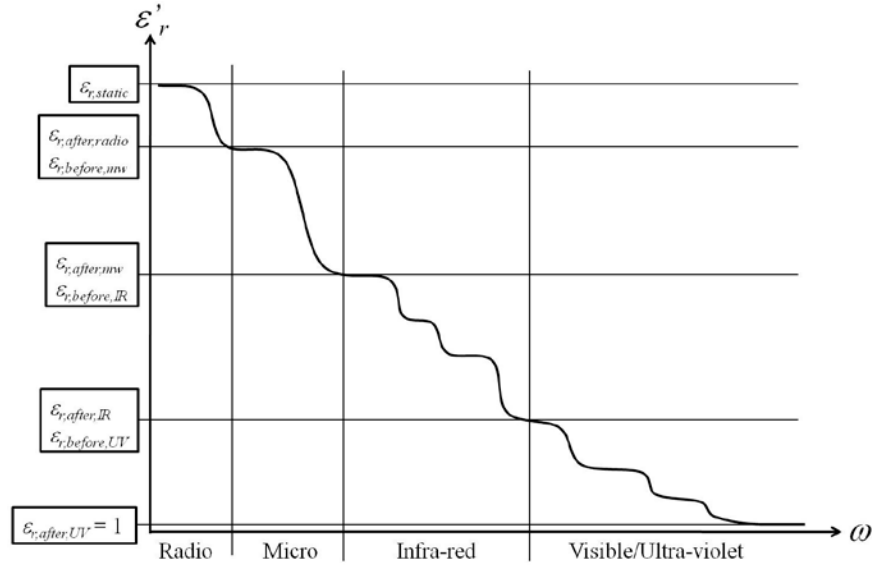


Figure 4. Schematic diagram demonstrating the physical significance of the dielectric dispersion properties used for calculations. The frequency axis is not drawn to scale.

6.0 Previous Approach to Approximate non-Retarded Hamaker Constant

The Pugh approximation is commonly used for a quick estimation of Hamaker constant as it only requires the relative static permittivity of the components rather than a dielectric dispersion representation of the species.¹⁴ The Pugh approximation is only able to deal with a single particle type system and is calculated by:

$$A_{131} = A_1 + A_3 - 2\sqrt{A_1 A_3} \quad (74)$$

Where the values of A_j ($j = 1$ or 3) are calculated by:

$$A_j = 113.7 K_B T \frac{(\epsilon_{r,static,j} - 1)^2}{(\epsilon_{r,static,j} + 1)^{3/2} (\epsilon_{r,static,j} + 2)^{1/2}} \quad (75)$$

6.1 *Characterization of the Mediums*

6.1.1 *Microwave Parameters*

The characteristic frequency (ω_{mw}) and the relative permittivity after the microwave relaxation ($\epsilon_{r,after,mw}$) was found in the literature for each medium.¹⁵ From this data, the characteristic oscillator strength of the microwave relaxation (C_{mw}) was calculated. There was no radio frequency relaxation for any material used in this study, therefore:

$$C_{mw} = \epsilon_{r,static} - \epsilon_{r,after,mw} \quad (76)$$

6.1.2 *Ultraviolet Parameters*

The ultraviolet/visible region was characterized by Cauchy plots for each medium except sec-butanol.¹⁶⁻²¹ Analysis of a Cauchy plot yields the characteristic ultraviolet/visible region oscillator strength (C_{UV}) and frequency (ω_{UV}) through the manipulation of refractive index data:²²

$$n'(\omega)^2 - 1 = (n'(\omega)^2 - 1) \frac{\omega^2}{\omega_{UV}^2} + C_{UV} \quad (77)$$

A plot of $n'(\omega)^2 - 1$ versus $\omega^2(n'(\omega)^2 - 1)$ will yield a straight line with the slope equal to $1/\omega_{UV}^2$ and a y-intercept equal to C_{UV} .

For sec-butanol, the first ionization potential was used to calculate the ultraviolet/visible spectroscopic properties because the refractive index data required for a Cauchy plot was unavailable. The frequency at the first ionization potential was used as the characteristic absorption frequency in the ultraviolet/visible region (ω_{UV}). As long as the absorption within the visible region is negligible, the characteristic oscillator strength (C_{UV}) in this region can be calculated by correlation with the refractive index at the sodium D line frequency:

$$C_{UV} = \epsilon_{r,before,UV} - \epsilon_{r,after,UV} = \epsilon_{r,after,IR} - \epsilon_{r,after,UV} = \epsilon_{r,after,IR} - 1 = n_s^2 - 1 \quad (78)$$

Therefore Equation 78 correctly assumes that after the ultraviolet relaxation, the relative permittivity of the material is unity and no polarization mechanisms can activate. Using the first ionization potential data (instead of the Cauchy plot method) values of ω_{UV} are systematically low while values for the oscillator strength, C_{UV} , are slightly high. Therefore the Cauchy method for determining ultraviolet/visible parameters is best, however if the data required for the Cauchy analysis is not available, the first ionization potential data can be used.

6.1.3 Infrared Parameters

The infrared characteristic absorption frequencies (ω_{IR}) were determined through Fourier transform infrared spectroscopy (FTIR).²³⁻²⁵ The total characteristic oscillator strength for the infrared region (C_{IR}) is a measure of the difference between the relative permittivity of the medium after the microwave relaxation ($\epsilon_{r,after,mw}$) and the relative permittivity of the medium after the infrared relaxation ($\epsilon_{r,after,IR}$):

$$C_{IR} = \epsilon_{r,after,mw} - \epsilon_{r,after,IR} \quad (79)$$

Since the relative permittivity of a material at frequencies higher than that of the ultraviolet relaxation frequency is unity, $\epsilon_r(\omega) \rightarrow 1$ as $\omega \rightarrow \infty$ (demonstrated in Equation 78) the total characteristic infrared oscillator strength can be calculated. The characteristic absorption strength of a specific frequency range (i.e. radio, microwave, infrared) is a measure of the loss of relative permittivity within that frequency range, therefore:

$$\epsilon_{r,static} = 1 + C_{UV} + C_{IR} + C_{mw} \quad (80)$$

Resulting in:

$$1 + C_{UV} = \epsilon_{r,before,UV} = \epsilon_{r,after,IR} = n_s^2 = \epsilon_{r,after,mw} - C_{IR} \quad (81)$$

From which the total characteristic oscillator strength for the infrared region, C_{IR} , can be calculated. For each medium there existed more than one major relaxation in the infrared region, a fraction of the total characteristic oscillator strength, c_{IR} , was assigned to each major oscillation based upon the bandwidth of the respective oscillation (Table V).

Table V. Dielectric Dispersion Properties of the Suspension Mediums

Suspending Medium	ω_{mw} (x 10 ¹⁰ rad/sec)	C_{mw}	ω_{IR} (x 10 ¹⁰ rad/sec)	C_{IR}	ω_{UV} (x 10 ¹⁰ rad/sec)	C_{UV}
Octanoic Acid	N/A	N/A	5.48	0.34	1.86	1.00
			3.23	0.04		
			2.93	0.01		
			2.71	0.04		
			2.31	0.07		
			1.75	0.03		
Poly(ethylene glycol)	N/A	N/A	5.45	10.26	1.87	1.10
			2.08	9.74		
Toluene	N/A	N/A	5.67	0.11	1.36	1.16
			5.43	0.01		
			3.03	0.01		
			2.78	0.04		
			1.36	0.04		
Heptane	N/A	N/A	5.49	0.01	1.87	0.89
			2.67	0.01		

Suspending Medium	ω_{mw} (x 10 ¹⁰ rad/sec)	C_{mw}	ω_{IR} (x 10 ¹⁰ rad/sec)	C_{IR}	ω_{UV} (x 10 ¹⁰ rad/sec)	C_{UV}
sec-Butanol	0.2	12.3	6.35	0.68	1.5	0.96
			5.5	0.34		
			2.68	0.24		
			2.12	0.16		
			1.94	0.02		
			1.87	0.05		
			1.72	0.05		
Isopropanol	0.34	15.22	6.32	0.51	1.76	0.87
			5.51	0.23		
			2.59	0.29		
			2.12	0.13		
			1.79	0.04		
			1.55	0.02		
Ethanol	0.78	20.1	6.28	1.11	1.91	0.83
			5.49	0.52		
			2.61	0.45		
			2.01	0.25		
			1.66	0.04		
Methanol	2.09	27.03	6.3	2.64	1.92	0.74
			5.53	0.64		
			5.34	0.15		
			1.94	0.43		

Suspending Medium	ω_{mw} (x 10 ¹⁰ rad/sec)	C_{mw}	ω_{IR} (x 10 ¹⁰ rad/sec)	C_{IR}	ω_{UV} (x 10 ¹⁰ rad/sec)	C_{UV}
2-Butanone	N/A	N/A	5.55	5.23	1.88	0.87
			3.24	2.85		
			2.64	5.47		
			2.22	2.38		
			1.77	0.43		
Acetone	31.26	18.8	3.25	0.03	1.82	0.82
			2.64	0.04		
			2.3	0.01		

One method to estimate the relative magnitude of the Hamaker constant with respect to suspending medium is to relate the refractive index of the medium to the magnitude.²⁶ It is proposed that a medium with a relatively low refractive index will generally induce a larger Hamaker constant than mediums with a larger refractive index. This concept is based upon the fact that larger refractive indices in effect renormalize the boundary between particles, this results in a larger separation distance between the respective colloids causing the attractive van der Waals dispersion force to be reduced. Figure 5 demonstrates that using the method described to discern the relative Hamaker constant between similar colloids in a suspension of the respective medium is not always valid since the colloids tested demonstrate that the non-retarded Hamaker constant is independent of the refractive index of the suspending medium.

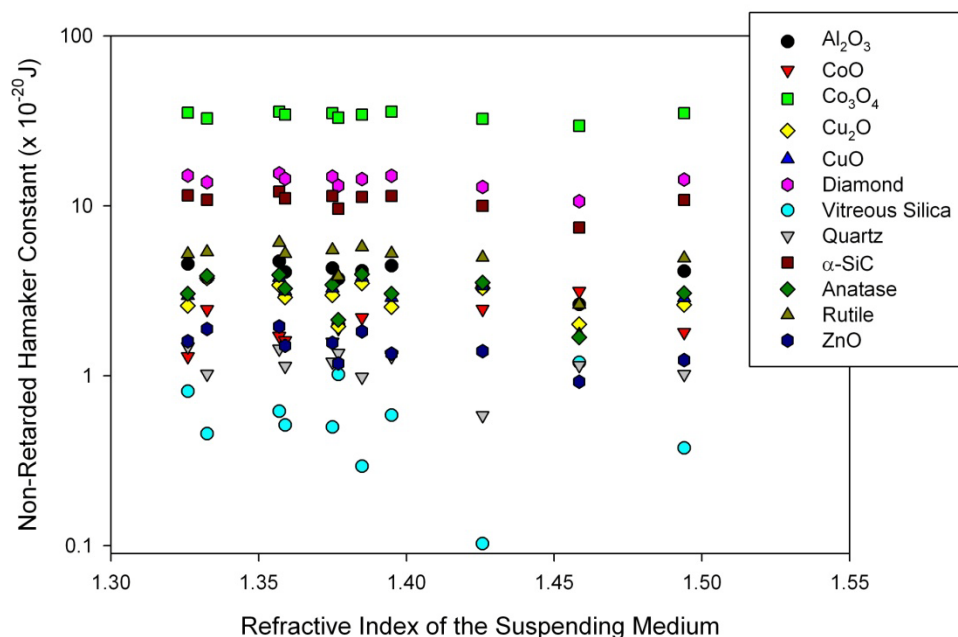


Figure 5. Non-retarded Hamaker constant as a function of the refractive index of the medium demonstrating that for some materials there is a correlation between the two.

The refractive index can be thought of as a measure of the electronic contribution to the dielectric dispersion of the material (ultraviolet frequency range) as long as no absorption is taking place at the frequency in which the refractive index was measured. Since no absorption is taking place:

$$\varepsilon(\omega) = \varepsilon'(\omega) = n'(\omega)^2 \quad (82)$$

If the square root of the refractive index is approximately equal to the relative static permittivity, the contribution of the frequencies less than ultraviolet frequencies is negligible. In these cases, the Hamaker constant may be approximated by the refractive index; however, the Hamaker constant is not only dependant on electronic dispersion (which is approximated by the refractive index) but also infrared and microwave dispersion. Therefore studying the correlation between Hamaker constant and refractive index of the medium will allow for determination of the relative influence that the electronic dispersion properties have upon the colloid in question.

6.2 *Characterization of Colloids*

For each medium, Hamaker constants were calculated for 12 different materials including diamond, alumina, cobalt (II) oxide, cobalt (II, III) oxide, alpha-silicon carbide, vitreous silica, quartz, anatase, rutile, copper (I) oxide, copper (II) oxide, and zinc oxide. The spectroscopic parameters for all powders can be found in Table VIII.

6.2.1 *Ultraviolet Parameters*

For most powders the parameters for the ultraviolet relaxations (ω_{UV} and C_{UV}) were determined via Cauchy plots.^{3,27,28} However, no spectral data were found with respect to anatase and Cu_2O . Since anatase (TiO_2) and Cu_2O are both semiconductors, there is limited (or no) refractive index data in the visible/near infrared region in which no absorption takes place ($n''(\omega)=0$). Therefore the bandgap of the material was used for the value of ω_{UV} (conversion shown in Equation 83) and C_{UV} was calculated in accordance with Equation 78.

$$\omega(\text{rad/sec}) = (1.53 \times 10^{15}) (\text{Bandgap (eV)}) \quad (83)$$

This approximation of the characteristic ultraviolet frequency was tested with materials that have a known ω_{UV} and bandgap. The characteristic frequencies were calculated for materials including quartz, Al_2O_3 , $\alpha\text{-SiC}$, diamond, and ZnO using the bandgap approximation (Table VI).

Table VI. Bandgaps of the Colloids Used to Determine the Applicability of the Bandgap Approximation

Material	Bandgap		Approximated ω_{UV} ($\times 10^{16}$ rad/sec)
	(eV)	Reference	
Al ₂ O ₃	8.8	29	1.34
Quartz	8.5	29	1.29
Diamond	5.4	29	0.820
CoO	4.0	29	0.608
ZnO	3.3	29	0.501
Rutile	3.0	30	0.456
α -SiC	2.9	29	0.441
CuO	1.2	28	0.182

Non-retarded Hamaker constants were calculated using the bandgap to approximate the ω_{UV} term. The results of the Hamaker constant calculation using the bandgap as an approximation for ω_{UV} were then correlated to the results of the Hamaker constant using the published values of ω_{UV} . Figure 6 demonstrates that the bandgap approach tends to underestimate the Hamaker constant compared to the Cauchy method. Therefore the bandgap approximation of ω_{UV} and subsequent calculation of Hamaker constant for oxide materials is observed to correlate well with the published values calculated using the Cauchy method. However, as demonstrated by diamond and α -SiC in Figure 7, using the bandgap to determine ω_{UV} for non-oxide materials does not seem to be suitable.

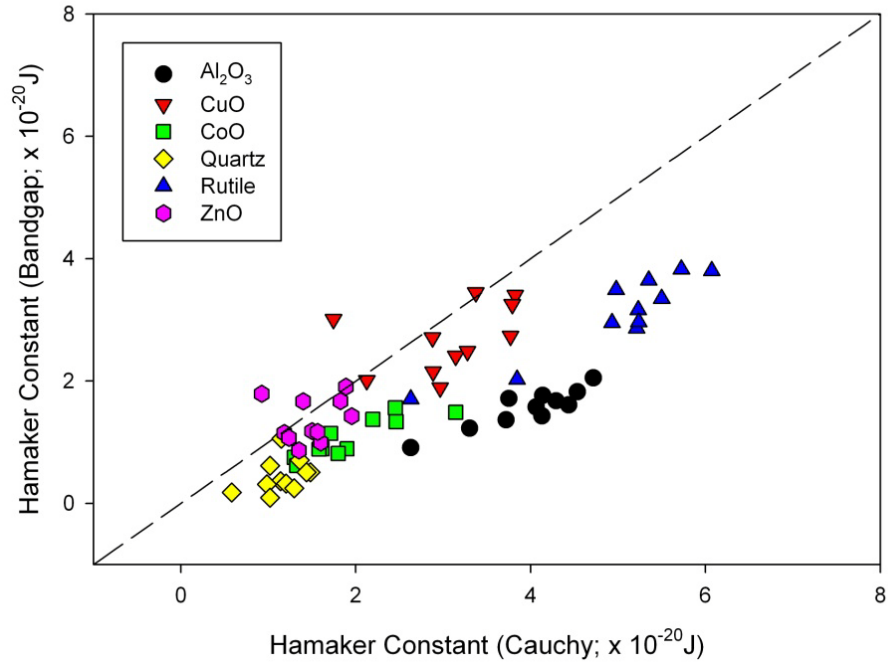


Figure 6. Correlation of the approximated Hamaker constant with the Hamaker constant using the accepted ω_{UV} value excluding the non-oxide materials. The dashed line represents the function $y = x$.

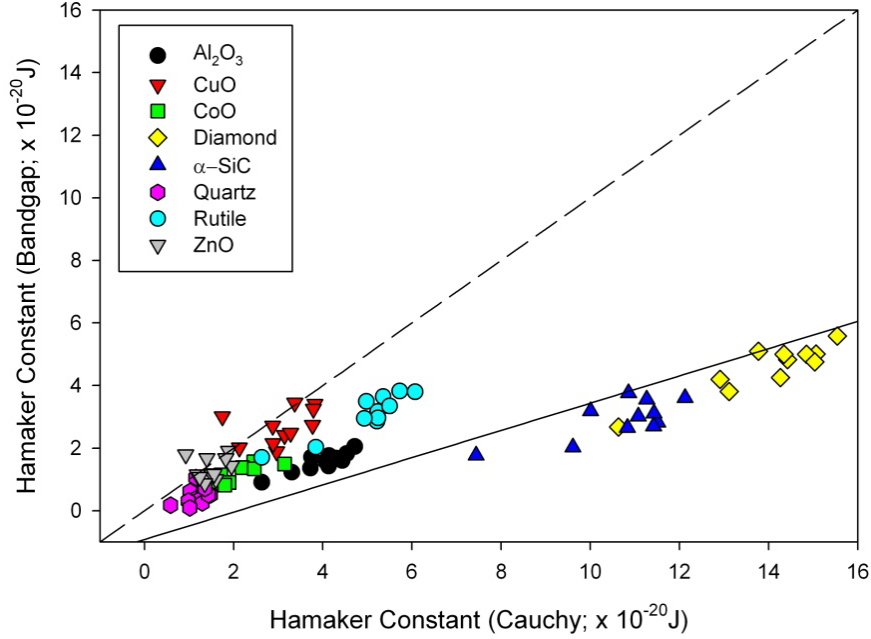


Figure 7. Correlation of the approximated Hamaker constant with the Hamaker constant using the accepted ω_{UV} value. The dashed line represents the function $y = x$ and the solid line represents the function $y = 0.44x - 0.91$.

Figure 7 shows that the bandgap significantly underestimates A for diamond and α -SiC. Since the non-oxide materials follow a linear trend, the observed underestimation can be corrected for:

$$A_{\text{Cauchy}} = \frac{A_{\text{Bandgap}} + 0.91}{0.44}$$

Figure 8 shows the comparison of the Pugh calculation with the full Lifshitz method and the bandgap approximation. Comparing the two methods, it can be observed that the Pugh approximation both over and under-estimates the Hamaker constant in all suspending mediums demonstrating no discernable trend while the bandgap approximation correlates well with the non-approximated values. The error associated with the Pugh approximation is an artifact of only using the static term in the calculations.

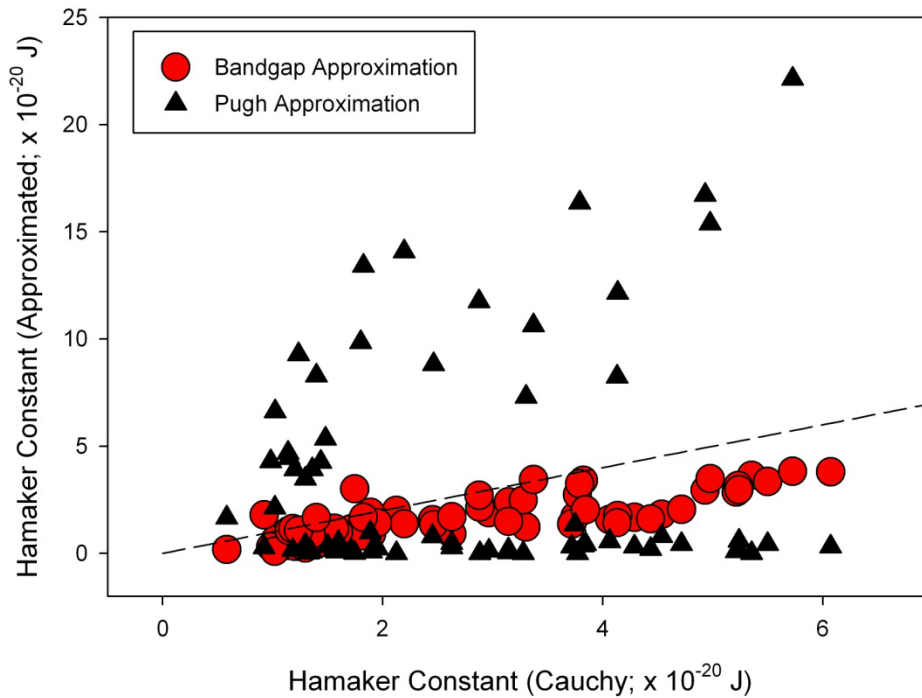


Figure 8. Comparison of non-retarded Hamaker constants calculated via the Pugh approximation and the bandgap approximation with the published values for oxide materials. The dashed line represents the function $y = x$.

6.2.2 Microwave Parameters

The inclusion of the microwave frequency range has been debated. Hough and White oppose the inclusion of the microwave relaxation term in the calculation of non-retarded Hamaker constants because it becomes the dominant term in $\varepsilon(i\xi)$ in the far ultraviolet frequencies where it should not exist.²² Although it is suggested by Hough and White to omit the microwave relaxation term it is still used.³ In this work, six of the 11 mediums did show a relaxation in the microwave frequency range which was included in the non-retarded Hamaker constant calculations. Table VII demonstrates that inclusion of the microwave term in the Hamaker constant calculations does not lead to a significant change in the value. The largest change was seen in water (at 11%) with the largest contributor being vitreous silica going from a value of $0.46 \times 10^{-20}\text{J}$ (microwave relaxation included) to $0.17 \times 10^{-20}\text{J}$ (excluding microwave relaxation). Colloids which demonstrated the most significant change with respect to the microwave relaxation include CuO, vitreous silica, quartz, and anatase.

Table VII. Comparison of Non-retarded Hamaker Constants Calculated With and Without the Microwave Relaxation Included. (A Negative Value Indicates a Decrease in the Non-retarded Hamaker Constant when the Microwave Relaxation is not Included in the Calculation.)

	Water	Methanol	Ethanol	Isopropanol	Sec-Butanol	Acetone
Al ₂ O ₃	-3.7%	-1.4%	0.00%	1.5%	1.4%	2.8%
CoO	-3.8%	-0.81%	3.3%	7.2%	7.9%	10.9%
Co ₃ O ₄	-0.20%	-0.03%	0.2%	0.32%	0.29%	0.54%
Cu ₂ O	-5.2%	-3.9%	-1.8%	0.16%	0.20%	1.8%
CuO	-7.5%	-8.5%	-5.9%	-4.6%	-5.7%	-2.7%
Diamond	-1.7%	-1.1%	-0.82%	-0.42%	-0.35%	-0.04%
α -SiC	-1.2%	-0.52%	0.02%	0.59%	0.56%	1.1%
Vitreous Silica	-62%	-25%	-34%	-27%	-20.9%	-19%
Quartz	-27%	-13%	-14%	-9.7%	-7.9%	-6.0%
Anatase	5.7%	9.0%	8.9%	9.1%	9.6%	9.8%
Rutile	5.8%	3.6%	3.2%	2.6%	2.3%	3.2%
ZnO	-5.7%	-1.9%	2.3%	6.2%	6.7%	8.2%
Average Difference	-11%	-6.1%	-6.6%	-5.8%	-5.1%	5.2%
C _{mw}	76.0	27.0	20.1	15.2	12.3	18.8

These differences may seem significant; however, once combined with the repulsive term to calculate the total interaction potential the difference becomes negligible. Figure 9 shows the total interaction potential as a function of separation distance for vitreous silica colloids in water. This system demonstrated the largest difference between the Hamaker constants calculated with and without the microwave term (approximately 30%). The difference in the plots is only noticeable when very small separation distances are realized, which does not affect the suspension stability prediction. Therefore, the microwave term may or may not be included in the Hamaker constant calculation without causing a significant change in the attractive potential.

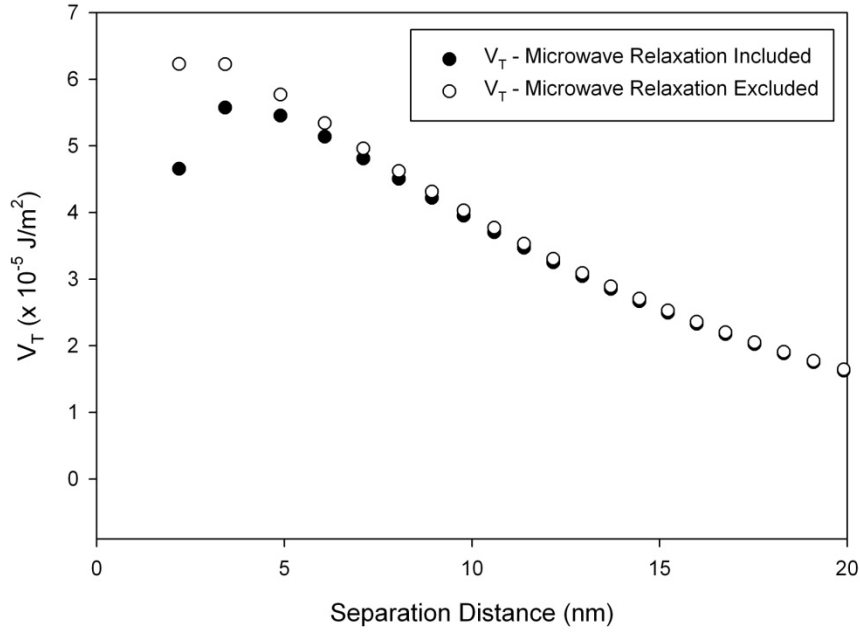


Figure 9. Comparison of total interaction potentials for vitreous silica as a function of separation distance in water.

The microwave relaxations were not used in the powder characterization, since most solids materials are not typically susceptible to molecular orientation. Therefore, C_{mw} was taken as zero resulting in:

$$\mathcal{E}_{r,static} = \mathcal{E}_{r,after,mw} \quad (84)$$

6.2.3 Infrared Parameters

For many of the materials, data for the infrared relaxations were available.³ However, when data were not, the parameters were determined in the same manner as for the mediums (using FTIR data).^{31,32} For the powders, the spectrum for each material was consolidated to include only a single characteristic frequency, ω_{IR} , corresponding to the largest absorption, in which the total characteristic oscillator strength, C_{IR} , was used. The total characteristic oscillator strength was calculated in the same manner as the mediums (Equation 81). Since it was assumed that the colloids tested do not demonstrate dielectric dispersion behavior in the microwave frequencies (Equation 84) it is found that:

$$C_{IR} = \varepsilon_{r,static} - \varepsilon_{r,after,IR} = \varepsilon_r - n_s^2 \quad (85)$$

Table VIII. Dielectric Dispersion Properties of the Powders Used in this Study

Chemistry	Mineralogy	ω_{IR} (x 10 ¹⁴ rad/sec)	C _{IR}	ω_{UV} (x 10 ¹⁶ rad/sec)	C _{UV}
Al ₂ O ₃	α	1.11	7.03	2.01 (Cauchy)	2.07 (Cauchy)
C	Diamond	2.50	0.02	1.61 (Cauchy)	4.64 (Cauchy)
CoO		1.11	9.73	0.33 (Cauchy)	2.17 (Cauchy)
Co ₃ O ₄		1.155	7.79	3.25 (Cauchy)	4.11 (Cauchy)
Cu ₂ O		1.15	0.26	0.33 (Bandgap)	6.34 Eq. 78
CuO		0.92	11.94	0.47 (Cauchy)	5.16 (Cauchy)
SiC	α	1.60	3.67	1.14 (Cauchy)	5.52 (Cauchy)
SiO ₂	Quartz	2.09	1.93	2.03 (Cauchy)	1.36 (Cauchy)
SiO ₂	Vitreous	1.47	1.72	2.03 (Cauchy)	1.10 (Cauchy)
TiO ₂	Anatase	1.13	24.65	0.50 (Bandgap)	5.35 Eq. 78
TiO ₂	Rutile	0.70	108.00	0.74 (Cauchy)	5.07 (Cauchy)
ZnO		0.70	8.15	0.90 (Cauchy)	2.65 (Cauchy)

The proposed method to determine the relative magnitude of the Hamaker constant with respect to different colloids is to observe the polarity of the bonds in the tested particles by examining the difference in electronegativity. From this observation a general pattern emerges for the oxide particles (Table IX). Lower values in the electronegativity difference between bound atoms (non-polar bonding) result in lower values of the Hamaker constant; as the difference in electronegativity between atoms increases so does the Hamaker constant. Therefore it is

hypothesized that the relative Hamaker constant can be approximated since generally increasing ionic character in the bonds of the particles leads to a larger Hamaker constant. This trend is true for the stoichiometric oxide particles. Diamond (non-oxide), α -SiC (non-oxide), and Co_3O_4 (non-stoichiometric) however do not follow this trend.

Table IX. Comparison of Non-retarded Hamaker Constant (at 298K) in Water with the Ionic Character of the Bond

Colloid	Ionic Character	A_{131} ($\times 10^{-20}$ J)
Vitreous Silica	1.54	0.46
Quartz	1.54	1.0
Cu_2O	1.54	3.7
CuO	1.54	3.8
CoO	1.56	2.5
ZnO	1.79	1.9
Al_2O_3	1.83	3.7
Anatase	1.90	3.9
Rutile	1.90	5.4
SiC	0.650	11
Diamond	0.00	14
Co_3O_4	1.56	33

This is consistent with the overall basis of the van der Waals force. The van der Waals force is a product of dipole interactions - the larger the dipole in an atom/molecule, the larger the interaction with other atoms/molecules and therefore the larger the resulting attractive force. Therefore it is hypothesized that for electrostatic stabilization, a large charge within the double-layer must be generated for particles such as titania whereas silica particles can be electrostatically dispersed with a significantly lower charge within the double-layer.

7.0 Hamaker Constant Calculations

Hamaker constants can be calculated using the Cauchy method, bandgap method, or the Pugh method. The Cauchy method uses a Cauchy plot to determine the ultraviolet/visible spectroscopic properties. The subsequent non-retarded Hamaker constant calculations are calculated in accord with the Lifshitz treatment using the Ninham-Parsegian damped oscillator

model for the dielectric dispersion data. The Cauchy method for calculating non-retarded Hamaker constants is generally accepted to be the most accurate. The Cauchy method requires the refractive index of the particle to be known as a function of wavelength at frequencies higher than the observed infrared absorption in a frequency range at which the absorption coefficient is negligible. This analysis is not trivial. The bandgap method described in this work uses the bandgap of the particle to approximate the ultraviolet/visible spectroscopic properties. This method generally underestimates the non-retarded Hamaker constants when compared to calculated values using the Cauchy method. Although the non-retarded Hamaker constants are underestimated, the bandgap approximated values follow a linear trend allowing for correction. Determination of the bandgap energy is a relatively simple process and for most materials the values are published. The Pugh approximation is the simplest of the three non-retarded Hamaker constant calculation methods requiring only the static dielectric terms of the particles and suspending medium to be known. The values of non-retarded Hamaker constant calculated using the Pugh method both underestimate and overestimate when compared to the values calculated using the Cauchy method. No discernable trend is observed to correct for the error when using the Pugh method.

Non-retarded Hamaker constants were calculated for each material in each medium using the Lifshitz treatment (Equation 72) with the Ninham-Parsegian representation of $\mathcal{A}(i\xi_n)$ (Equation 73) and are tabulated in Table X. The spectroscopic properties used in the calculations are tabulated in Table V and Table VIII. For all mediums the Cauchy method was used with the exception of sec-butanol in which the first ionization potential was used because of the lack of available refractive index data (Table V). Table VIII shows that the Cauchy method was used for determination of the ultraviolet/visible parameters for most particles, however for anatase and Cu_2O the data required for Cauchy analysis was not available and the bandgap method was used.

Table X. Non-retarded Hamaker Constants ($\times 10^{-20}$ J) for the Selected Materials in the Various Mediums at 298K

	Vacuum (Air)	Water	Methanol	Ethanol	IPA	Sec- Butanol	Acetone	MEK	Heptane	Toluene	Octanoic Acid	PEG
ZnO	9.21	1.89	1.60	1.50	1.56	1.35	1.95	1.18	1.82	1.24	1.40	0.92
Rutile	15.3	5.35	5.21	5.23	5.50	5.24	6.07	3.84	5.72	4.93	4.98	2.63
Anatase	10.6	3.87	3.05	3.26	3.43	3.05	3.92	2.14	3.96	3.06	3.53	1.68
SiC	24.9	10.9	11.5	11.1	11.4	11.4	12.1	9.61	11.3	10.8	10.0	7.44
Quartz	8.86	1.02	1.48	1.14	1.20	1.30	1.44	1.36	0.980	1.02	0.580	1.15
Vitreous Silica	6.50	0.460	0.810	0.510	0.50	0.590	0.620	1.02	0.290	0.380	0.100	1.20
Diamond	29.6	13.8	15.1	14.4	14.9	15.0	15.5	13.1	14.4	14.3	12.9	10.6
CuO	10.3	3.82	2.96	3.14	3.28	2.88	3.77	2.12	3.79	2.88	3.37	1.74
Cu ₂ O	8.17	3.75	2.58	2.89	2.98	2.54	3.42	1.95	3.50	2.61	3.28	2.01
Co ₃ O ₄	53.0	32.7	35.3	34.4	35.1	35.8	35.8	33.0	34.4	35.1	32.5	29.6
CoO	2.98	2.45	1.30	1.61	1.58	1.32	1.71	1.90	2.20	1.80	2.46	3.14
Al ₂ O ₃	15.3	3.75	4.53	4.06	4.29	4.43	4.72	3.72	4.14	4.13	3.30	2.63

Table X illustrates that the effect of particle type is much greater than the effect of suspending medium. The range of Hamaker constant values for a single particle type in the various suspending mediums (excluding vacuum) is 2.70×10^{-20} J, while the range of Hamaker constant for a single suspending medium with different particles is 33.4×10^{-20} J. Based on the Hamaker constants, it is seen that silica (both vitreous and quartz) generate a weak van der Waals attractive force between particles whereas the Co_3O_4 generates the largest van der Waals force.

8.0 Conclusions

Determination of the spectral parameters required for the Ninham-Parsegian damped oscillator model were done by previously proven methods; however, a newly determined method was employed for materials. For semiconductors, approximation of the ultraviolet spectral parameters using the bandgap produced a negligible difference in Hamaker constant when compared with the Cauchy method. The Hamaker constant is most sensitive to the ultraviolet region of the electromagnetic spectrum (~70% of the value comes from the ultraviolet region) thus allowing for a very good approximation of the Hamaker constant for newly developed materials based solely upon bandgap and index of refraction measurements (neglecting the microwave and infrared contributions of the particle to the Hamaker constant). The relative influence that the microwave and infrared dispersions have on the Hamaker constant of the colloid may be discerned through correlation of the Hamaker constant and the refractive index of the material. A good correlation suggests that the contributions of all non-electronic dispersions are negligible. However, this correlation will only be valid if all frequencies are considered in the calculation of the Hamaker constant.

The systems with the smallest values of non-retarded Hamaker constant and subsequent van der Waals attractive potential were identified as potential candidate systems for electrostatic stabilization. The two silica particles (quartz and vitreous) demonstrated the smallest attractive potentials of the nine particle types in all mediums. The diamond and Co_3O_4 particles possess the largest values of the Hamaker constant. A trend between the ionic character of the bond and Hamaker constant was observed only for stoichiometric oxide particles which made intuitive sense – the more ionic (polar) the bond, the larger the calculated Hamaker constant and therefore subsequent attractive potential. Hamaker constants approximated by the Pugh relationship are consistently overestimated.

9.0 List of Variables

A – Hamaker constant

A_{131} – Hamaker constant between colloids of material type 1 with intervening medium (3)

A_j – Hamaker constant of material j in the Pugh approximation

C_{mw} – Characteristic oscillator strength of the microwave frequency range

C_{IR} – Characteristic oscillator strength of the infrared frequency range

C_{UV} – Characteristic oscillator strength of the ultraviolet frequency range

C_j – Characteristic oscillator strength of the infrared or ultraviolet frequency range

D – Separation distance

K_B – Boltzmann's constant

n – Integer

n' – Real refractive index (transmission)

n'' – Imaginary refractive index (absorption)

n_s – Real refractive index at the sodium D line

V_A – Total van der Waals attractive potential

Δ_{ij} – Difference in dielectric dispersion between materials i and j

$\epsilon_{r,static}$ – Relative static permittivity

ϵ_r – Relative permittivity

$\epsilon(\omega)$ – Complex permittivity as a function of real frequency

$\epsilon'(\omega)$ – Real permittivity as a function of real frequency (transmission)

$\epsilon''(\omega)$ – Imaginary permittivity as a function of real frequency (absorption)

$\epsilon(i\xi_n)$ – Permittivity as a function of imaginary frequency

ξ_n – Imaginary frequency

ω – Real frequency

ω_{mw} – Characteristic frequency of the microwave frequency range

ω_R – Characteristic frequency of the infrared frequency range

ω_{UV} – Characteristic frequency of the ultraviolet frequency range

ω_j – Characteristic frequency of the infrared or ultraviolet frequency range

ν – Integer

10.0 References

1. H.C. Hamaker, "The London-van der Waals Attraction between Spherical Particles," *Physica*, **4**, 1058-72 (1937).
2. L.D. Landau, L.P. Pitaevskii, and E.M. Lifshitz, *Electrodynamics of Continuous Media*, 2nd ed., Vol. 8; p. 460. Edited by L. D. Landau and E. M. Lifshitz. Butterworth-Heinemann, Oxford, England, 1984.
3. L. Bergstrom, "Hamaker Constants of Inorganic Materials," *Adv. Colloid Interface Sci.*, **70**, 125-69 (1997).
4. R.M. Pashley, "The van der Waals Interaction for Liquid Water: A Comparison of the Oscillator Model Approximation and Use of the Kramers-Kronig Equation with Full Spectral Data," *J. Colloid Interface Sci.*, **62** [2] 344-7 (1977).
5. C.M. Roth and A.M. Lenhoff, "Improved Parametric Representation of Water Dielectric Data for Lifshitz Theory Calculations," *J. Colloid Interface Sci.*, **179** [2] 637-9 (1996).
6. D.C. Prieve and W.B. Russel, "Simplified Predictions of Hamaker Constants from Lifshitz Theory," *J. Colloid Interface Sci.*, **125** [1] 1-13 (1988).
7. E.M. Lifshitz, "The Theory of Molecular Attraction Forces between Solid Bodies," *Sov. Phys. JETP*, **2**, 73-83 (1956).
8. B.W. Ninham and V.A. Parsegian, "van der Waals Forces across Triple-Layer Films," *J. Chem. Phys.*, **52** [9] 4578-87 (1970).
9. L.R. White, R.R. Dagastine, P.M. Jones, and Y.-T. Hsia, "van der Waals Force Calculation between Laminated Media, Pertinent to the Magnetic Storage Head-Disk Interface," *J. Appl. Phys.*, **97** [10] 104503-7 (2005).
10. W.D. Callister, *Materials Science and Engineering: An Introduction*, 6th ed.; p. 820. John Wiley & Sons, New York, 2003.
11. L.V. Azaroff and J.J. Brophy, *Electronic Processes in Materials*; p. 462. McGraw-Hill, New York, 1963.

12. L. Solymar and D. Walsh, *Electrical Properties of Materials*, 7th ed.; p. 402. Oxford University Press, New York, 2004.
13. B.W. Ninham and V.A. Parsegian, "van der Waals Forces: Special Characteristics in Lipid-Water Systems and a General Method of Calculation Based on the Lifshitz Theory," *Biophys. J.*, **10** [7] 646-63 (1970).
14. R.J. Pugh, "Dispersion and Stability of Ceramic Powders in Liquids," pp. 127-92 in *Surfactant Science Series*, Vol. 51, *Surface and Colloid Chemistry in Advanced Ceramics Processing*. Edited by R. J. Pugh and L. Bergstrom. Marcel Dekker, New York, 1994.
15. F. Buckley and A.A. Maryott, "Tables of Dielectric Dispersion Data for Pure Liquids and Dilute Solutions," National Bureau of Standards Circular 589 (U.S.), 1958.
16. T. Masuda, Y. Matsuki, and T. Shimoda, "Spectral Parameters and Hamaker Constants of Silicon Hydride Compounds and Organic Solvents," *J. Colloid Interface Sci.*, **340** [2] 298-305 (2009).
17. E. Moreels, C. de Greef, and R. Finsy, "Laser Light Refractometer," *Appl. Opt.*, **23** [17] 3010-3 (1984).
18. K. Kerl and H. Varchmin, "Refractive Index Dispersion (RID) of Some Liquids in the UV/Vis between 20°C and 60°C," *J. Mol. Struct.*, **349**, 257-60 (1995).
19. J.E.F. Rubio, J.M. Arsuaga, M. Taravillo, V.G. Baonza, and M. Cáceres, "Refractive Index of Benzene and Methyl Derivatives: Temperature and Wavelength Dependencies," *Exp. Therm. Fluid Sci.*, **28** [8] 887-91 (2004).
20. J.E.F. Rubio, J.M. Arsuaga, M. Taravillo, and M. Cáceres, "Refractive Index Temperature and Wavelength Dependencies of Normal Saturated Fatty Acids in Liquid State," *Exp. Therm. Fluid Sci.*, **29** [6] 681-4 (2005).
21. I.Z. Kozma, P. Krok, and E. Riedle, "Direct Measurement of the Group-Velocity Mismatch and Derivation of the Refractive-Index Dispersion for a Variety of Solvents in the Ultraviolet," *J. Opt. Soc. Am. B*, **22** [7] 1479-85 (2005).
22. D.B. Hough and L.R. White, "The Calculation of Hamaker Constants from Lifshitz Theory with Applications to Wetting Phenomena," *Adv. Colloid Interface Sci.*, **14** [1] 3-41 (1980).
23. C.J. Pouchert, *The Aldrich Library of Infrared Spectra*, 3rd ed. Aldrich Chemical, Milwaukee, WI, 1981.
24. "Evaluated Infrared Reference Spectra" National Institute of Standards and Technology. Accessed on: October 26, 2010. Available at <<http://webbook.nist.gov>>

25. F.F. Bentley, L.D. Smithson, and A.L. Rozek, *Infrared Spectra and Characteristic Frequencies (700-300cm⁻¹) Collection of Spectra, Interpretation, and Bibliography*; p. 457. Interscience Publishers, New York, 1968.
26. R.H. French, "Origins and Applications of London Dispersion Forces and Hamaker Constants in Ceramics," *J. Am. Ceram. Soc.*, **83** [9] 2117-46 (2000).
27. K.M. Andersson and L. Bergström, "DLVO Interactions of Tungsten Oxide and Cobalt Oxide Surfaces Measured with the Colloidal Probe Technique," *J. Colloid Interface Sci.*, **246** [2] 309-15 (2002).
28. E.D. Palik, *Handbook of Optical Constants of Solids*, Vol. II; p. 1096. Academic Press, New York, 1991.
29. Y.-M. Chiang, D.B. III, and W.D. Kingery, *Physical Ceramics: Principles for Ceramic Science and Engineering*; p. 522. John Wiley & Sons, New York, 1997.
30. H. Tang, K. Prasad, R. Sanjines, P.E. Schmid, and F. Levy, "Electrical and Optical Properties of TiO₂ Anatase Thin Films," *J. Appl. Phys.*, **75** [4] 2042 (1994).
31. R.A. Nyquist and R.O. Kagel, *Infrared Spectra of Inorganic Compounds (3800-45cm⁻¹)*, Vol. 4; p. 500. 1972.
32. *Sadtler High Resolution Spectra of Inorganics and Related Compounds*. Sadtler Research Laboratories, Philadelphia, 1967.

III. PAPER #2

1.0 Title

Exact DLVO Calculations of Non-aqueous Suspensions

Keith J. DeCarlo

William M. Carty

2.0 Keywords

Double-layer, Non-aqueous, Inorganic Colloids

3.0 Abstract

DLVO theory was used to calculate the electrostatic repulsive force for 15 different colloids in 13 different suspending mediums. Electrostatic potentials were calculated using the exact solution of the Poisson-Boltzmann differential equation. By using the area hyperbolic tangent function the electrostatic potential term was isolated. Subsequent interaction potential calculations were completed using elliptical integrals. Based on the repulsive potential data, it is hypothesized that all colloids tested which were suspended in heptane and toluene require the addition of a surfactant in order to induce stability. All colloids suspended in acetone, methanol, and ethanol are theorized to induce electrostatic dispersion without the requirement of additives. The other suspension mediums had mixed results and the potential for a stable suspension was found to be dependent on the colloid.

4.0 Introduction

The stability of lyophobic colloids in a liquid medium has been successfully modeled through DLVO theory.¹ DLVO theory is based upon the observation that colloidal particles interact via repulsive and attractive interparticle forces which are electrostatic in nature. DLVO theory has been applied almost exclusively to water based systems in which direct force measurements have proven the validity of the theory.² When applied to systems which use organic liquids as the suspension medium, DLVO theory has been observed to fail.³ It is because of the failures of

DLVO theory in this regard that led to the assumption that other forces are present (or not present) when using suspension mediums other than water.⁴

Although DLVO theory has been observed to fail when studying non-aqueous suspensions, the same interparticle forces must develop. Much like when introduced into water, colloids develop surface charges in organic media (regardless of polarity) and therefore develop a double-layer due to association of free ions in solution.⁵⁻¹⁴ Development of the surface charge in water and other polar media (relative static permittivity, $\epsilon_{r,static} > 15$) has been well studied and understood, however the development of surface charges in non-polar media (relative static permittivity, $\epsilon_{r,static} < 15$) is not as well understood – based on the difficulty to reach dispersion it is hypothesized that ions may not be ionized from the particle surface or the ions do not reach the degree of complexation required to prevent spontaneous coalescence and therefore do not form a sufficiently charged double-layer. Charge on the particle surface and a subsequent double-layer, however has been observed in non-polar mediums with no added electrolyte.^{6,11,13}

The charged double-layer developed by particles when introduced to a medium is the basis for the electrostatic repulsive forces. These repulsive forces develop in accordance to the overlap of the two interacting double-layers. A repulsive force is developed based on electrostatics; particles become electrostatically dispersed when the repulsive charges are large enough to overcome the intrinsic van der Waals attractive force between particles. Polar mediums allow for larger ionic double-layers to develop due mainly to the associated relative static permittivity of the respective medium. The large relative static permittivity, commonly referred to as the dielectric constant, of polar media allows for ions at relatively large distances away from the particle surface to be incorporated into the respective ionic double-layer. In non-polar mediums, ions are not as easily associated to the double-layer at large distances away from the particle surface. This leads to a large charge gradient in non-polar mediums (the charge quickly decays away from the particle surface towards the bulk suspension) requiring the particles to be closer together before the double-layers interact. The closer in proximity the particles are with respect to each other, the larger the van der Waals attractive force between the particles (van der Waals force is proportional to D^{-6}).^{11,12} Therefore the requirements for electrostatic stability are not only a sufficient charge on the particle (measured as ζ -potential), but also a small charge gradient away from the particle surface towards the bulk suspension.

Although the charge gradient and size of the double-layer are important, ζ -potential has been commonly used as the sole metric to predict dispersion. It is a common misconception that a large measured ζ -potential will result in dispersion. This has even led to an ASTM standard

(now defunct) to be written in accord with this misconception.¹⁵ Furthermore, it is often seen that large ζ -potential values can be observed without dispersion especially in non-polar solvents.

5.0 Experimental

Experiments were completed using various suspension mediums which included methanol, ethanol, isopropanol, sec-butanol, acetone, 2-butanone (Methyl Ethyl Ketone), toluene, heptane, octanoic acid, 200 molecular weight poly(ethylene glycol), and water. 2-Butanone and poly(ethylene glycol) will be referred to as MEK and PEG respectively. All organic mediums used were characterized as anhydrous by the supplier. Suspensions were prepared in a N₂ backfilled glovebox in order to reduce the interaction of the medium with the water vapor in the air. In all, 15 different powders were tested in each medium including diamond, alumina, cobalt metal, cobalt (II, III) oxide, silica, titania, copper metal, copper (I) oxide, and copper (II) oxide. All powders were characterized and the results are listed in Table XII.

Table XI. Suspension Medium Properties

Suspending Medium	Relative Static Permittivity, $\epsilon_{r,static}$		Viscosity, η (mPa·s at 298K)
	At 298K	Reference	
Heptane	1.90	16	0.39
Toluene	2.40	17	0.56
Octanoic Acid	2.50	16	5.0
sec-Butanol	15.8	17	3.1
MEK	18.2	18	0.41
Isopropanol	18.3	17	2.0
Acetone	20.7	17	0.32
PEG	22.1	19	50.
Ethanol	24.3	17	1.1
Methanol	32.6	17	0.55
Water	78.5	17	0.89

Table XII. Characterization of the Powders Used in this Study. Powder Manufactures Include Diamond Innovations (*), Umicore (+), Sigma Aldrich ($\perp$), Aluchem ($\otimes$), Ceralox ($\oplus$), Sumitomo ($\oslash$), Alpha Aesar ($\diamond$).

Powder	Designation	ID	ρ (g/cm ³)	SSA (m ² /g)	Calculated PS ₅₀ (μ m)
C (*)	Diamond	D-1A	3.54	4.2	0.40
C (*)	Diamond	D-2A	3.55	1.9	0.89
C (*)	Heat Treated Diamond	D-2T	3.54	1.8	0.94
Co (+)	Jet Milled	Co	8.19	3.2	0.23
Co ₃ O ₄ ($\perp$)		Co ₃ O ₄	6.04	0.78	1.3
Al ₂ O ₃ ($\otimes$)	AC16SG	A-AC	4.01	9.9	0.15
Al ₂ O ₃ ($\oplus$)	HPA-1.0	A-HPA	3.96	4.7	0.32
Al ₂ O ₃ ($\oslash$)	AKP30	A-AKP	4.00	6.9	0.22
SiO ₂ ($\diamond$)	Quartz	Quartz	2.68	5.7	0.39
SiO ₂ ($\diamond$)	Vitreous	Vitreous Silica	1.96	8.5	0.36
TiO ₂ ($\diamond$)	Anatase	Anatase	3.92	10.	0.15
TiO ₂ ($\diamond$)	Rutile	Rutile	4.43	4.6	0.29
Cu ($\diamond$)		Cu	8.36	1.5	0.48
Cu ₂ O ($\perp$)		Cu ₂ O	6.01	0.49	2.0
CuO ($\perp$)		CuO	6.31	1.5	0.63

The specific surface area (SSA) of each powder was determined via N₂-BET analysis (TriStar 3000, Micromeritics, Norcross, GA, USA). Samples were initially dried and degassed for one hour in the sample tube before the analysis by heating to 150°C under a dynamic nitrogen atmosphere. The Co sample was degassed but not heated due to the flammable nature of the powder.

The bulk density of each powder was measured using a pycnometer method (AccuPyc 1330 He-pycnometer, Micromeritics, Norcross, GA, USA). At least three measurements were made for each sample for statistical purposes. Each sample underwent five purging cycles prior to measurement.

The median particle size was estimated using Equation 86. This approach assumes that the particle is spherical and completely smooth (all variables are defined at the end of the chapter).

$$PS_{50} = \frac{6}{\rho(SSA)} \quad (86)$$

A microelectrophoretic laser method (Model 501 Lazer Zee Meter™, Pen Kem Inc., Bedford Hills, NY, USA) was used to measure ζ -potential rather than the more commonly used acoustophoretic mobility approach. The advantage of the laser method is that it allows for the direct observation of particle mobility in an applied electric field. Testing required a minimum of 10^6 particles/ml and a maximum of 10^9 particles/ml. Therefore, the solids loading of the suspensions varied due to density and particle size. Each suspension was sealed in a polyethylene tetrathalate (PET) bottle to minimize evaporation and stored in a fume hood. It was assumed that the solvents did not significantly interact with the PET containers. The Lazer Zee Meter used to measure ζ -potential was calibrated to measure colloids in water at 298K. To correct for both temperature (Equation 87) and suspension medium properties (Equation 88), correction factors were given by the manufacturer.

$$\zeta_{\text{corrected}} = \zeta_{\text{measured}} [1.4 - (0.016)(T - 273)] \quad (87)$$

$$\zeta_{\text{corrected}} = \zeta_{\text{measured}} \left(\frac{\epsilon_{r,static,water}}{\epsilon_{r,static,medium}} \right) \left(\frac{\eta_{medium}}{\eta_{water}} \right) \quad (88)$$

Before each measurement, the instrument was reset to the zero-velocity plane within the sample holder. The location of zero-velocity plane was determined from the thickness of the sample holder and the magnification power of the objective lens. All suspensions were tested at five different voltages to generate an associated standard deviation (Figure 10), in two separate experiments. If the two measurements were not within a 99% confidence interval the suspensions were re-measured until repeatability was observed.

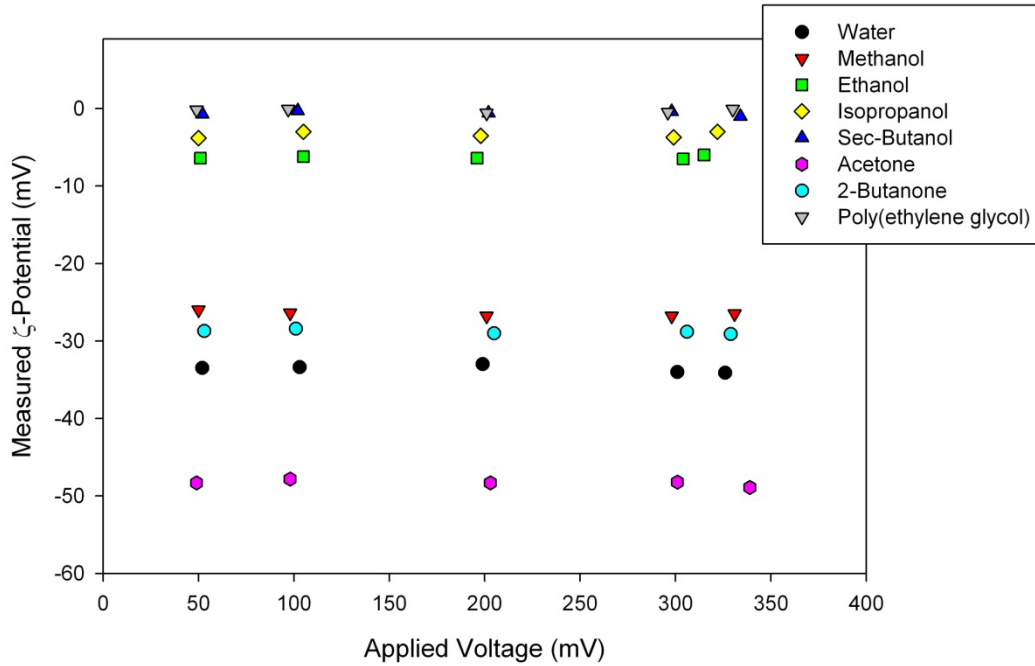


Figure 10. Measured ζ -potential as a function of applied voltage for vitreous silica in all mediums that resulted in a non-zero ζ -potential.

6.0 Results and Discussion

The Debye-length ($L = 1/\kappa$) was calculated for each medium (Table XIII). The Debye-length is a function of the suspension medium, electrolyte concentration, and the type of electrolyte and is independent of the type of colloid.

$$\kappa = \sqrt{\frac{e^2}{\epsilon_{r,static} \epsilon_o K_B T} \sum_i 1000 M_i N_A z_i^2} \quad (89)$$

All calculations were conducted using a temperature value of 298K with monovalent symmetrical salts at a concentration of 1.0mM. Although this assumption does not seem valid with non-polar mediums, in which electrolyte dissociation is less pronounced, some ion concentration is necessary to calculate Debye-length. The calculated Debye-length for each medium is presented in Table XIII.

Table XIII. Calculated Debye-lengths of Particles in the Selected Suspension Mediums Assuming Symmetrical Electrolytes with a Valence of $z=1$.

Suspending Medium	Relative Static Permittivity, $\epsilon_{r,static}$	Debye-length, L (nm)			
		100mM	10mM	1.0mM	0.1mM
Heptane	1.9	0.15	0.47	1.5	4.7
Toluene	2.4	0.17	0.53	1.7	5.3
Octanoic Acid	2.5	0.17	0.54	1.7	5.4
Sec-Butanol	15.8	0.43	1.4	4.3	14
MEK	18.2	0.46	1.5	4.6	15
Isopropanol	18.3	0.46	1.5	4.6	15
Acetone	20.7	0.49	1.6	4.9	16
PEG	22.1	0.51	1.6	5.1	16
Ethanol	24.3	0.54	1.7	5.4	17
Methanol	32.6	0.62	2.0	6.2	20.
Water	78.5	0.96	3.0	9.6	30.

Table XIII demonstrates that the Debye-length increases as the ionic concentration decreases, as would be expected. For non-polar mediums such as heptane, toluene, and octanoic acid, the change in the Debye-length with changing ionic concentration is less significant than the polar mediums. For each medium, the Debye-length changes by approximately a factor of three with a change in the order of magnitude of ionic strength, although changing the Debye-length will not change the prediction of relative potential for stability based on the electrostatic behavior of the suspension. An assumption of 1.0mM for the ionic strength of all mediums allowed for each calculated potential to be consistent relative to the other mediums. Figure 11 illustrates the change graphically, which demonstrates that the trend in general appears to be true and the dependence on ionic strength decreases with decreasing polarity. Water is the medium most significantly affected by the ionic concentration, thus making the assumption of a 1.0mM ionic concentration for each medium acceptable.

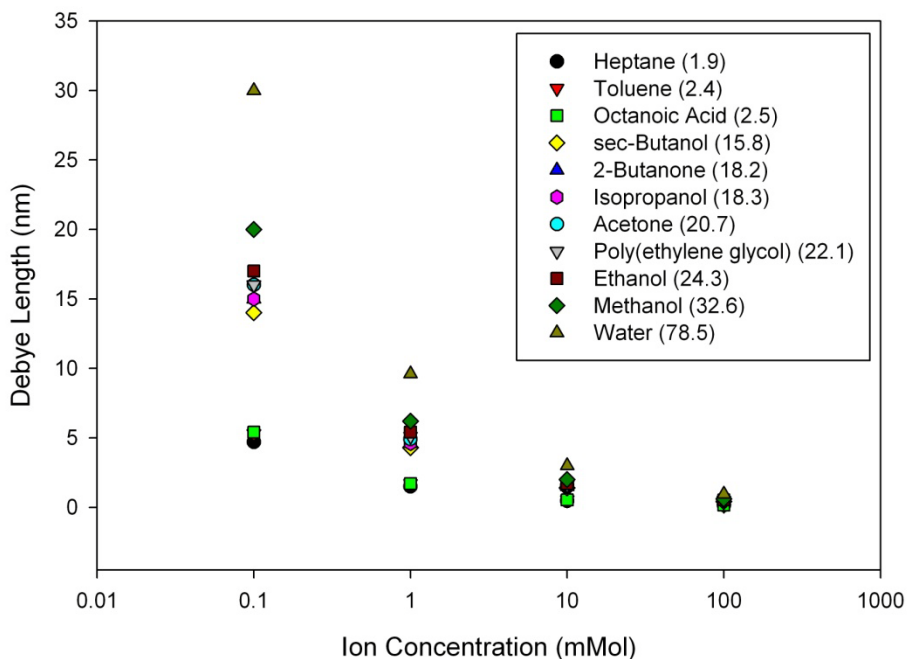


Figure 11. Graphical representation of the effect that ion concentration has on the Debye-length. The static dielectric constant is noted in parentheses.

The thickness of the double-layer is an important aspect with regards to the repulsive potential. The larger the double-layer, the farther apart the particles will be when double-layers begin to interact. Table XIII implies that water will be the best medium for inducing electrostatic dispersion and heptane will be the worst. Polar suspending mediums allow for the particle to associate ions to the double-layer more easily than non-polar mediums which is demonstrated in Table XIII and Equation 89 by the direct proportion between relative dielectric constant and Debye-length. This is due to the ability of a medium to translate the charge away from the particle surface through the polarizability of the medium. From the calculated values, it is observed that the thickness of the double-layer formed in a non-polar medium is much smaller than that formed in a polar medium, requiring particles to move closer together before double-layer interaction occurs. This leads to the conclusion that dispersion of particles is more easily accomplished in mediums with a high relative static permittivity.

Although Debye-length does give a rough estimation of the ability of a particle to be dispersed without a sufficient charge within the double-layer, dispersion will not occur even if the Debye-length is large. To measure the particle surface charge, ζ -potentials were measured for each

colloid/medium combination and then corrected for medium and temperature using Equations 87 and 88 (Table XIV).

Table XIV. ζ -potential Values (mV) for Each Powder in Each Solvent.

	Water	Methanol	Ethanol	Isopropanol	Acetone	MEK	PEG	Sec-Butanol	Heptane	Toluene	Octanoic Acid
Rutile	-38.6	-2.00	-32.4	-29.3	-41.2	-47.2	-33.1	3.70	56.2	13.7	150
Anatase	-42.2	-40.0	-26.0	-0.900	-41.6	-73.1	-16.2	15.2	113	0.000	84.3
Quartz	-36.4	-5.00	-38.0	-28.0	-58.9	-62.0	0.000	-10.6	23.3	41.4	0.000
Vitreous Silica	-33.1	-40.9	-25.3	-33.4	-69.3	-56.2	-50.7	-10.1	0.000	0.000	0.000
CuO	-26.5	-28.9	-51.9	-34.8	-40.9	-29.5	-19.6	18.3	0.00	-8.60	18.0
Cu ₂ O	-29.5	-2.70	-20.4	-22.0	-26.1	-16.5	179	33.3	3.80	126	54.0
Cu	-42.6	14.9	28.9	-48.3	-38.5	-28.3	-15.3	21.3	-1.60	0.000	33.8
Co ₃ O ₄	-48.0	-15.0	-4.7.0	-55.8	7.30	-31.5	0.000	25.7	-9.70	-37.7	-36.9
Co	13.8	-25.9	-30.1	-26.7	-24.9	-65.8	68.0	14.9	30.6	92.3	29.0
A-AC	26.5	-8.00	-11.2	-18.5	-54.2	-36.7	-23.6	28.1	71.5	0.000	0.000
A-HPA	17.4	-15.4	-12.1	-22.3	-75.3	-40.2	-75.9	13.0	107	-40.4	0.000
A-AKP	27.2	-9.10	-10.6	-13.4	-69.1	-60.9	-18.4	35.6	15.0	-14.0	37.0

In some medium-particle couples no charge was observed; it is obvious that particles of that type cannot be dispersed electrostatically in the respective medium and therefore do not require further analysis. Although the suspending medium does make a significant contribution to the magnitude of the charge generated, the suspension medium is most significant when comparing the sign of the charge generated. All powders tested, with the exception of vitreous silica, exhibited charge reversal based on the medium used. This is most likely a consequence of the charge generation mechanism, as the change in the charge is generally observed when comparing non-polar solvents to polar mediums (sec-butanol is of intermediate polarity). It is important to note that ζ -potential can only be used to predict colloidal stability in cases where the dispersion mechanism is electrostatic in nature. If the stabilization mechanism includes a steric effect, the ζ -potential data will not likely correlate with the degree of dispersion.

The diffuse double-layer electrostatic potential (ψ) is defined in Equation 90. Equation 90 is derived from the Poisson-Boltzmann differential equation. It is common to study colloidal suspensions using a reduced potential term, ψ_R , which is a dimensionless quantity equal to $e\psi/K_BT$.

$$\tanh\left(\frac{ze\psi}{4K_BT}\right) = \tanh\left(\frac{ze\zeta}{4K_BT}\right) \exp[-\kappa_s(x-d)] \quad (90)$$

Although this is how colloidal suspensions are studied, it would be more direct (and tangible) to solve Equation 90 for the diffuse double-layer electrostatic potential. It can be shown that by using the area hyperbolic tangent function (artanh), the electrostatic potential can be solved for analytically:

$$\psi = \frac{4K_BT}{ze} \operatorname{artanh}\left[\tanh\left(\frac{ze\zeta}{4K_BT}\right) \exp[-\kappa(x-d)]\right] \quad (91)$$

The diffuse double-layer electrostatic potential has been calculated for each powder type in every solvent as a function of distance. Figure 12 shows the response of alumina (A-AKP) in selected

suspension mediums. Although not all responses were included, the mediums shown were selected in order to show the range of behavior.

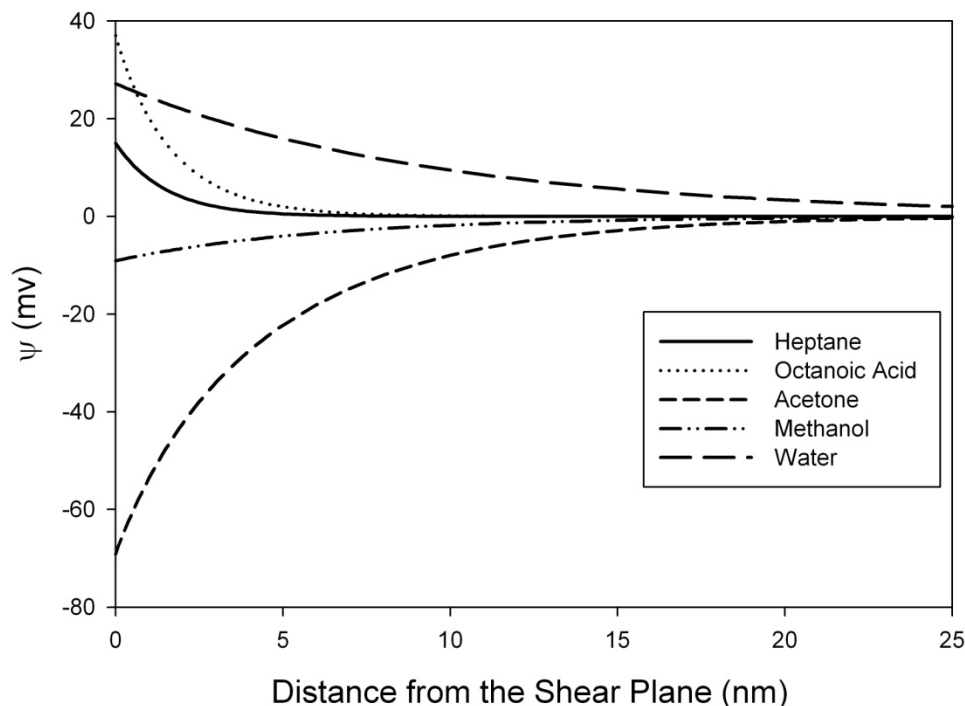


Figure 12. Electrostatic potential as a function of distance for A-AKP in selected mediums.

In all samples tested it was observed that water has the shallowest diffuse double-layer electrostatic potential gradient. This is due to water having the largest relative static permittivity (78.5 at 298K) of all mediums tested, resulting in the largest double-layer. Heptane and other non-polar solvents had a steep diffuse double-layer electrostatic potential gradient. These large gradients observed are a direct result of the Debye-length – the larger the double-layer, the more associated charge within it. Although larger ζ -potential values were sometimes observed in the non-polar mediums, the large associated charge gradient means that the charge rapidly decays as the distance from the shear plane increases requiring smaller separation distances for double-layer interaction between particles.

When two particles interact, the diffuse double-layer electrostatic potential changes. At large separation distances (distances close to that of the Debye-length) the cumulative electrostatic

potential is simply additive; however, when the separation distance between particles decreases, the cumulative electrostatic potential is more complex. The shape of the diffuse double-layer interaction potential curve is limited by the Poisson differential equation:

$$\frac{d^2\psi}{dx^2} = \frac{-\rho}{\epsilon_{r,static}\epsilon_o} \quad (92)$$

Solving Equation 92 for the total separation distance results in an elliptical integral. Elliptical integrals cannot be solved analytically; however, tables of solutions have been compiled. The solution to Equation 92 fit to the general formula of an elliptical integral is:

$$D = 4\kappa_s^{-1} \exp(k) \left[F\left(\frac{\pi}{2}, k\right) - F(\phi, k) \right] \quad (93)$$

Where k and ϕ are defined as:

$$k = \exp(-u) \quad (94)$$

$$\phi = \cos^{-1} \left[\exp\left(\frac{(\psi_m - \zeta)ze}{2K_B T}\right) \right] \quad (95)$$

From Equation 93, the diffuse double-layer interaction potential at the mid-point plane can be calculated as a function of particle separation distance. This has been calculated for like particles in the various mediums based on the measured ζ -potential values. Figure 13 shows graphs of the interaction of the alumina colloids depicted in Figure 12 with each other in selected mediums.

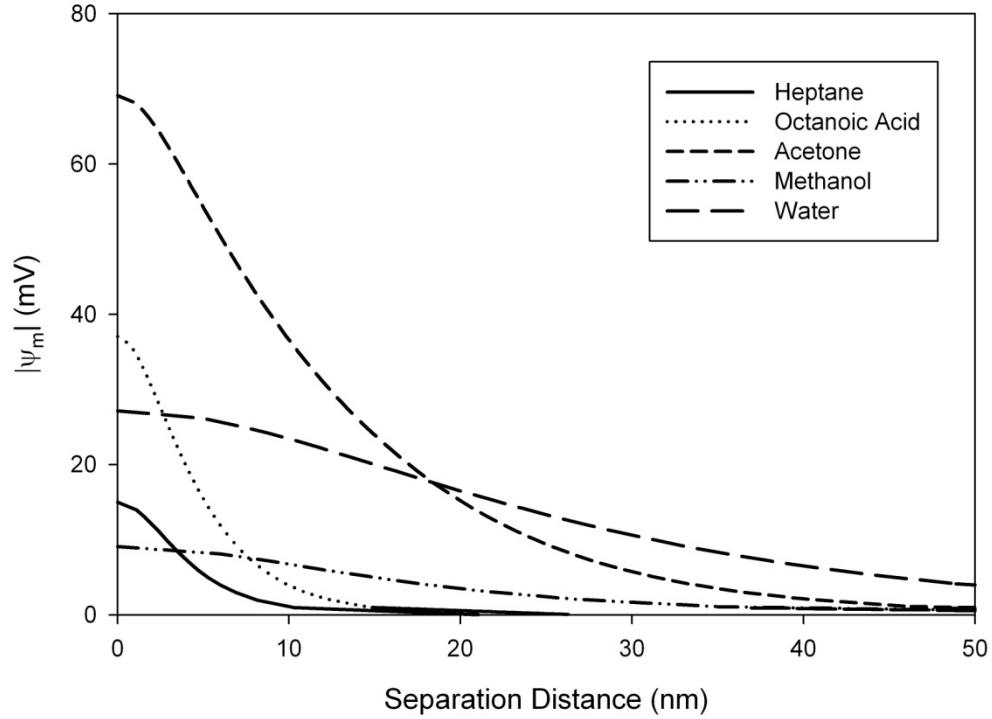


Figure 13. Effect of two interacting colloids on the (net) electrostatic potential as a function of separation distance for A-AKP in selected mediums.

It is observed that a significant charge is generated in water at relatively large separation distances when compared to the other solvents. Non-polar solvents require a small separation distance between interacting particles to generate an electrostatic response. This results in the requirement of a much larger repulsive potential to overcome the van der Waals force of attraction than that required for polar solvents.

The repulsive potential generated from two interacting particles is analyzed by calculation of osmotic pressure developed because of the accumulation of ions between particles:

$$V_R = 2(U_m - U_\infty) \quad (96)$$

U_m is defined as:

$$U_m = -2n^o K_B T \kappa_s^{-1} \left[\frac{D}{4\kappa_s^{-1}} (3\exp(u) - 2 - \exp(-u)) + 2\sqrt{2\cosh(b) - 2\cosh(u)} + I \right] \quad (97)$$

Which the second order elliptical integral in Equation 97 is equivalent to:

$$I = 2 \int_u^b \frac{\exp(-y) - \exp(u)}{\sqrt{2\cosh(y) - 2\cosh(u)}} dy \quad (98)$$

Solutions to Equation 98 cannot be calculated analytically, yet can be determined by using the tables of compiled solutions. To use the tables of solutions, Equation 98 must be put into the form:

$$I = -2 \exp\left(\frac{u}{2}\right) \left[E\left(\frac{\pi}{2}, \exp(-u)\right) - E\left(\sin^{-1}\left[\exp\left(-\frac{b-u}{2}\right)\right], \exp(-u)\right) \right] \quad (99)$$

Substituting Equation 99 into Equation 97, U_m can be determined. U_∞ can be found by restricting Equation 97 to the case of the bulk suspension ($m \rightarrow \infty$) which results in the explicit expression:

$$U_\infty = -2n^o K_B T \kappa_s^{-1} \left[4 \cosh\left(\frac{b}{2}\right) - 4 \right] \quad (100)$$

With both U_m and U_∞ able to be solved, the total repulsive potential between two interacting particles can now be calculated explicitly by substituting Equations 100 and 97 into Equation 96.

Repulsive potential data for all colloid/medium couples have been calculated. Figure 14 shows the repulsive potential as a function of interparticle separation distance for the colloid/medium couples depicted in Figure 12 and Figure 13.

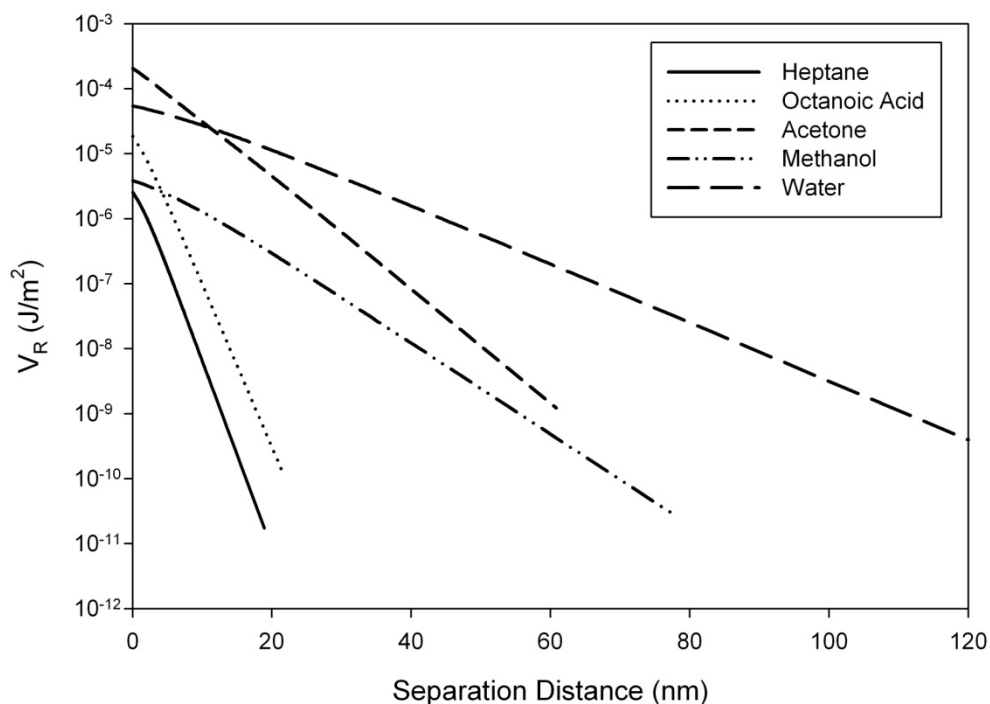


Figure 14. Calculated repulsive potential as a function of separation distance for A-AKP in selected mediums.

Figure 14 shows that polar mediums generally begin to generate a repulsive potential between like particles at larger separation distances relative to polar mediums. A repulsive force is required in order to counteract the intrinsic van der Waals attractive force. If the developed repulsive force is not large enough to counteract the attractive force the particles will agglomerate. The attractive force has a large dependence on separation distance; therefore, the larger the separation distance between particles when a significant repulsive force is developed, the more likely the suspended colloids will be dispersed (stable). Therefore, based on Figure 14, the best candidate suspension mediums would be those that are polar. It is interesting to note that even though large ζ -potentials were observed in non-polar mediums ($\zeta > 100\text{mV}$, Table XIV) such as anatase in heptane ($\zeta = 112.5\text{mV}$), the repulsive potentials produced in these situations are not large and require particles to be close together before a significant potential is formed. For anatase in methanol the ζ -potential is significantly smaller ($\zeta = -40\text{mV}$), however the repulsive potential is much more significant and has a larger range.

Based solely on the repulsive potential data, a number of potential candidate systems for dispersion in the specific medium have been identified. All colloidal suspensions using

methanol or ethanol as the medium are proposed to be dispersed. Isopropanol, sec-Butanol, acetone, and 2-butanone also have good dispersion characteristics based upon the repulsive potential data. Using isopropanol as the medium, only anatase is hypothesized to agglomerate whereas the other colloids should be dispersed. For the case of sec-butanol, acetone, and 2-butanone, only the heat-treated diamond is hypothesized to agglomerate. When poly(ethylene glycol) is used as the suspending medium, all colloids are hypothesized to be dispersed with the exception of Co_3O_4 and quartz. Suspensions made using heptane, toluene, or octanoic acid as the suspending medium demonstrated that, according to the repulsive potential data, most colloids tested would agglomerate. The only colloids that are hypothesized to be dispersed in the non-polar mediums include: Co_3O_4 , heat treated diamond, and rutile. From the poor dispersibility demonstrated by the heptane, toluene, and octanoic acid, it can be established that the suspended colloids will not generate a charge within the double-layer sufficient enough to cause electrostatic dispersion. In these solvents the double-layer thickness is relatively small as is (in most cases) the charge generated. Even when large charges are generated, the repulsive force generated is still much smaller than other solvents (Figure 14); this can be attributed to the double-layer thickness. All colloids suspended in acetone, methanol, or ethanol demonstrate a significant repulsive potential and therefore are hypothesized as universal mediums – allowing for dispersion of every colloidal system studied. Although the candidate systems are chosen via the repulsive potential it is only a hypothesis because the total interaction potential is needed to fully characterize a system which is calculated with both the repulsive potential and the attractive potential.

7.0 Conclusions

The repulsive potentials of colloidal suspension systems using a variety of mediums were characterized. It was observed that the double-layer thickness correlated with the relative static dielectric constant of the suspending medium – polar mediums ($\epsilon_{r,static} > 15$) generated a large double-layer while the double-layer formed in non-polar mediums was much smaller. A large double-layer was generated in polar mediums because the relative static dielectric constant of the medium allowed for ions further from the colloid surface to be associated within the double-layer. The larger the double-layer, the better the expected dispersibility of the colloids via an electrostatic mechanism. With a larger double-layer, a repulsive potential will be generated at larger separation distances between particles. A large separation distance between particles is necessary because as the particles become closer together the larger the attractive van der Waals

force becomes. In addition to a large double-layer it is also necessary to induce a charge on the particle (measured via ζ -potential). A large charge correlates to a large repulsive potential when the respective colloids interact. Large ζ -potentials were observed in both polar and non-polar mediums. For colloids which developed a thick double-layer, the charge density was also large implying that the charge gradient ($d\psi/dx$ from the colloidal surface towards the bulk of the suspension) was relatively small. In contrast, colloids which developed a smaller double-layer (non-polar mediums) had a smaller charge density and therefore a large charge gradient (the charge decreased rapidly from the colloidal surface). Potential candidate systems for dispersion have been identified by observing the generation of the repulsive potential. It is hypothesized that heptane and toluene will not cause a stable suspension without the use of a surfactant, while every colloid tested in acetone, methanol, and ethanol developed a large repulsive potential which may translate into suspension stability without requiring the use of surfactants. To fully characterize the systems for electrostatic stability, attractive potentials must be calculated and compared to the repulsive potentials calculated in this study.

8.0 List of Variables

$$b = \frac{ze\zeta}{K_B T}$$

D – Total separation distance

d – Distance from the particle surface to the shear plane

e – Charge on an electron

I – Second order elliptical integral

K_B – Boltzmann's constant

L – Debye-length

M_i – Molarity of ion i

m – Distance from the particle surface to the mid-point plane

N_A – Avogadro's number

n_i – Number of ion of type i in the double-layer

n_i^o – Number of ion of type i in the bulk suspension per unit volume

p – Osmotic pressure

PS_{50} – Median Particle Size

R – Gas constant

SSA – Specific Surface Area

T – Temperature

U_m – Free energy at the mid-point plane between interacting particles

U_∞ – Free energy of the bulk suspension

$$u - \frac{ze\psi_m}{K_B T}$$

V_R – Repulsive potential

x – Distance from the particle surface

$$y - \frac{ze\psi}{K_B T}$$

z_i – Valence of ion i

$\epsilon_{r,static}$ – Relative static permittivity (Dielectric constant)

ϵ_o – Permittivity of a vacuum

κ^{-1} – Debye-length

κ_s^{-1} – Debye-length only including symmetrical electrolytes

η – Viscosity at 298K

ρ – Density

ψ – Electrostatic potential

ψ_r – Reduced potential

ψ_m – Electrostatic potential at the mid-point plane

ζ – ζ -potential

9.0 References

1. E.J.W. Verwey and J.T.G. Overbeek, *Theory of the Stability of Lyophobic Colloids*; p. 205. Elsevier, New York, 1948.
2. D. Chan and P. Richmond, "Van der Waals Forces for Mica and Quartz: Calculations from Complete Dielectric Data," *Proc. R. Soc. London, A*, **353** [1673] 163-76 (1977).
3. F.J. Rubio-Hernandez, "Is DLVO Theory Valid for Non-Aqueous Suspensions?" *J. Non-Equilib. Thermodyn.*, **24** [1] 75-9 (1999).
4. B.W. Ninham, "On Progress in Forces since the DLVO Theory," *Adv. Colloid Interface Sci.*, **83** [1-3] 1-17 (1999).
5. A. Kitahara, "Stability of Dispersions in Polar Media," *Adv. Colloid Interface Sci.*, **38**, 1-11 (1992).
6. I.D. Morrison, "Electrical Charges in Nonaqueous Media," *Colloids Surf., A*, **71** [1] 1- (1993).
7. F. Boschini, A. Rulmont, R. Cloots, and R. Moreno, "Rheological Behaviour of BaZrO₃ Suspensions in Non-Aqueous Media," *Ceram. Int.*, **35** [3] 1007-13 (2009).
8. J.M. Thwala, J.W. Goodwin, and P.D. Mills, "Electrokinetic Studies of Colloidal Silica Particles Dispersed in Non-Aqueous Media in the Presence of a Nonionic Surfactant, Dodecylhexaethylene Glycol Monoether (C₁₂E₆)," *Colloids Surf., A*, **335** [1-3] 33-42 (2009).
9. W. Wang, S. Martin-Moe, C. Pan, L. Musza, and Y.J. Wang, "Stabilization of a Polypeptide in Non-Aqueous Solvents," *Int. J. Pharm.*, **351** [1-2] 1-7 (2008).
10. U. Paik, V.A. Hackley, S.-C. Choi, and Y.-G. Jung, "The Effect of Electrostatic Repulsive Forces on the Stability of BaTiO₃ Particles Suspended in Non-Aqueous Media," *Colloids Surf., A*, **135** [1-3] 77-88 (1998).
11. R.J. Pugh, "Dispersion and Stability of Ceramic Powders in Liquids," pp. 127-92 in Surfactant Science Series, Vol. 51, *Surface and Colloid Chemistry in Advanced Ceramics Processing*. Edited by R. J. Pugh and L. Bergstrom. Marcel Dekker, New York, 1994.
12. P.C. van der Hoeven and J. Lyklema, "Electrostatic Stabilization in Non-Aqueous Media," *Adv. Colloid Interface Sci.*, **42**, 205-77 (1992).
13. R. Xu, C. Wu, and H. Xu, "Particle Size and Zeta Potential of Carbon Black in Liquid Media," *Carbon*, **45** [14] 2806-9 (2007).

14. R.O. James, "Characterization of Colloids in Aqueous Systems," pp. 349-410 in *Advances in Ceramics*, Vol. 21, *Ceramic Powder Science*. Edited by G. L. Messing, J. W. McCauley, and K. S. Mazdidasni. American Ceramic Society, Westerville, OH, 1987.
15. "Zeta Potential of Colloids in Water and Waste Water" ASTM Designation D 4187-82. American Society for Testing Materials, West Conshohocken, PA.
16. C. Wohlfarth, *Static Dielectric Constants of Pure Liquids and Binary Liquid Mixtures*. Edited by M. D. Lechner. Springer-VDI-Verlag, Düsseldorf, Germany, 1991.
17. *CRC Handbook of Chemistry and Physics*, 70th ed. Edited by D.R. Lide CRC Press, New York, 1990.
18. R.H. Cole, "Dielectric Constants of Aliphatic Ketones," *J. Chem. Phys.*, **9** [3] 251-7 (1941).
19. R.J. Sengwa, K. Kaur, and R. Chaudhary, "Dielectric Properties of Low Molecular Weight Poly(ethylene glycol)s," *Polym. Int.*, **49** [6] 599-608 (2000).

IV. PAPER #3

1.0 Title

Rheology of Colloids in Non-aqueous Suspensions and Determination of the Stability Mechanism

Keith J. DeCarlo

William M. Carty

2.0 Keywords

Viscosity, Non-aqueous, Dispersion, Agglomeration, Stability

3.0 Abstract

The viscosity of 165 suspensions (11 mediums x 15 types of colloids) was tested. The viscosity was used to measure the interactions between the particles in suspension. It was determined that the majority of the suspensions tested were agglomerated (unstable). The best suspension tested for inducing dispersion is poly(ethylene glycol) based on the viscosity measurements. The applicability of DLVO theory requires suspensions to be stabilized by an electrostatic mechanism with no other mechanisms having a significant impact in dispersion. The mechanism of dispersion is hypothesized to be able to be determined by comparison of the specific viscosity of the suspension at a shear rate of 1.0s^{-1} with the shear thinning exponent. It was determined that all suspensions with the exception of those prepared with heptane, octanoic acid, and poly(ethylene glycol) all had an electrostatic dispersion mechanism with no other mechanisms operating in a significant capacity. Therefore it is hypothesized that the suspension stability for the suspensions tested except for those with poly(ethylene glycol), heptane, and octanoic acid can be predicted by DLVO theory.

4.0 Introduction

Viscosity is commonly used to screen for dispersed suspensions. The viscosity of a suspension (η) as a function of shear rate ($\dot{\gamma}$) can be described via a power law model over a broad range of shear rates:

$$\log \eta = \log \eta_{1.0} - \mathbf{n} \log \gamma \quad (101)$$

Where $\eta_{1.0}$ is the viscosity of the suspension at a shear rate of 1.0s^{-1} and $\mathbf{n}$ is the shear thinning exponent. Because suspensions exhibit shear thinning behavior, the shear rate for comparison is critical. At high shear rates the data converges to infinity whereas lower shear rates better demonstrate viscosity differences. Therefore the suspension stability is defined by the viscosity at a shear rate of 1.0s^{-1} . Based on previous work, the viscosity cutoff for stability was determined to be $\eta_{1.0} = 10^4\text{mPa}\cdot\text{s}$; therefore if $\eta_{1.0} < 10^4\text{mPa}\cdot\text{s}$ the suspension is described as dispersed.¹ When comparing the viscosity of suspensions using different suspending mediums it is useful to define the specific viscosity (η_{specific}):²

$$\eta_{\text{specific}} = \frac{\eta_{1.0}}{\eta_{\text{medium}}} \quad (102)$$

Where η_{medium} is the intrinsic viscosity of the suspending medium. By using the specific viscosity, the rheology of the suspending medium is normalized to the viscosity of the medium and therefore allows for the rheology of suspensions using different mediums to be compared to one another. Using the specific viscosity to define the cut-off viscosity, the cut-off is found to be 1.1×10^4 .

Although viscosity can be used to determine the suspension stability, a method for determining the mechanism of dispersion has yet to be determined. Knowing the mechanism of dispersion will allow for the understanding of why specific stability models are applicable or not. The most robust stability model is DLVO theory; however, it only applies to suspensions dispersed electrostatically. This fact has proven to cause confusion and it is hypothesized that the reported “non-DLVO” forces existing in non-aqueous suspensions are forces introduced through other stabilization mechanisms present.^{3,4}

5.0 Experimental

Viscosity was measured using a strain-controlled rheometer (ARES-RFS, Rheometric Scientific Inc., Piscataway, NJ, USA) with parallel plate geometry (nominal gap of approximately 10^3

times larger than the particle size) for all 165 suspensions (11 mediums x 15 colloid types). The suspending mediums tested include water, methanol, ethanol, isopropanol, sec-butanol, acetone, 2-butanone (methyl ethyl ketone), heptane, toluene, octanoic acid, and 200 molecular weight poly(ethylene glycol). 2-Butanone and poly(ethylene glycol) will be referred to as MEK and PEG respectively. The properties of each medium are listed in Table XV.

Table XV. Properties of Each of the Suspending Mediums Used. The Organic Suspending Mediums are Arranged in Increasing Order of Viscosity.

Suspending Medium	Viscosity, η At 298K⁵	Chemical Class	Functional Group	Structure
Acetone	0.32	Ketone	Carbonyl	Aliphatic
Heptane	0.39	Alkane	N/A	Aliphatic
2-Butanone	0.41	Ketone	Carbonyl	Aliphatic
Methanol	0.55	Alcohol	Hydroxyl	Aliphatic
Toluene	0.56	N/A	Phenyl	Aromatic
Ethanol	1.1	Alcohol	Hydroxyl	Aliphatic
Isopropanol	2.0	Alcohol	Hydroxyl	Aliphatic
sec-Butanol	3.1	Alcohol	Hydroxyl	Aliphatic
Octanoic Acid	5.0	Carboxylic Acid	Carboxyl	Aliphatic
Poly(ethylene glycol)	50.	Polymer	Hydroxyl	Aliphatic
Water	0.89	N/A	N/A	N/A

The colloids tested included α -alumina, diamond, cobalt metal, cobalt (II,III) oxide, copper metal, copper (I) oxide, copper (II) oxide, quartz, vitreous silica, rutile, and anatase. Characterization experiments for colloids were reported previously. The properties of each colloid are presented in Table XVI.

Table XVI. Characterization of the Colloids Used in the Suspensions

Chemistry	ID	Measured Density (g/ml)	Specific Surface Area (m ² /g)	Calculated PS ₅₀ (μm)
Al ₂ O ₃	A-AC	4.01	9.89	0.15
Al ₂ O ₃	A-HPA	3.96	4.72	0.32
Al ₂ O ₃	A-AKP	4.00	6.90	0.22
Co	Co	8.19	3.16	0.23
Co ₃ O ₄	Co ₃ O ₄	6.04	0.78	1.27
Cu	Cu	8.36	1.53	0.47
Cu ₂ O	Cu ₂ O	6.01	0.49	2.0
CuO	CuO	6.31	1.51	0.63
SiO ₂ (Quartz)	Quartz	2.68	5.71	0.39
SiO ₂ (Vitreous)	Vitreous Silica	1.96	8.45	0.36
TiO ₂ (Anatase)	Anatase	3.92	10.04	0.15
TiO ₂ (Rutile)	Rutile	4.43	4.59	0.30

Each suspension prepared had a total volume of 30ml and was 20vol% solids. Prior to the measurement, each suspension was ultrasonicated for one minute while submerged in an ice bath to reduce vaporization of the solvent. Each viscosity measurements required 10ml of suspension which was taken from the bulk suspension after ultrasonification. A shear-rate sweep starting at 10s⁻¹ to 0.1s⁻¹ was used with a pre-shear step of three seconds at 10s⁻¹. The measurement time varied based on the time to reach a steady-state viscosity and the geometry of the plates varied based on the viscosity of the suspension being tested. For low viscosity suspensions a 50mm plate was used; for high viscosity suspensions a 25mm plate was used. A temperature of 298K was maintained using a peltier heater and water bath. The resulting data was analyzed using instrument software and a spreadsheet.

6.0 Results and Discussion

6.1 *Rheology of the Suspensions*

Viscosity is being used as a metric to define the interactions between the particles in suspension. Suspension viscosity is a function of five variables:⁶

1. Particle-particle interactions
2. Solids loading
3. Particle size and distribution
4. Particle morphology
5. Rheology of the suspension medium

The first variable, particle-particle interactions, has the greatest effect on the viscosity. If the colloids act independently and do not form agglomerates, the suspension is described as stable (dispersed). Conversely, if the colloids form agglomerates and subsequently settle out of the suspension the suspension is described as unstable (flocculated). The other four variables do not affect the viscosity to the same degree that the particle-particle interactions do, however in order to distinguish the interactions between the suspended colloids using viscosity measurements, the other four variables must be accounted for. The solids concentration of each suspension was known, therefore allowing the variable to be accounted for. All particles were selected to have similar sizes (Table XVI). The particle size was logarithmically distributed for all powders since they were synthesized from a top-down process (i.e. grinding, milling). The top-down synthesis process used to synthesize all powders used will also result in similar morphologies. The suspension medium viscosity was accounted for by using the specific viscosity (Equation 102) to describe the suspension viscosity rather than the measured viscosity. The viscosity of all suspending mediums tested can be described as Newtonian (independent of shear rate). The specific viscosity stability cut-off value is defined to be 1.1×10^4 .

The measured viscosity of each suspension was modeled via the power law (Equation 101) using a regression method (Figure 15). In all cases the R^2 value was $R^2 > 0.95$.

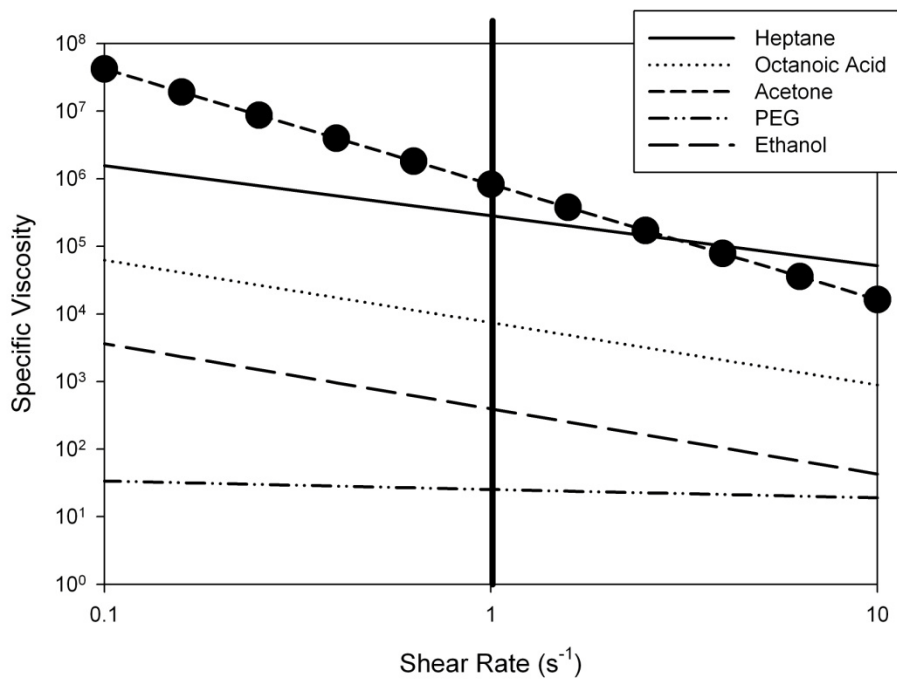


Figure 15. Specific viscosity as a function of shear rate for vitreous silica in selected mediums.

The suspension stability was defined by the viscosity at a shear rate of 1.0s^{-1} , which corresponds to the y-intercept in Equation 101. Therefore, Figure 15 demonstrates that using acetone results in an unstable suspension and using PEG results in a stable suspension for vitreous silica. The specific viscosity for each suspension at a shear rate of 1.0s^{-1} is compiled in Table XVII.

Table XVII. Specific Viscosity ($\times 10^3$) at a Shear Rate of 1.0s^{-1} for Each Suspension Tested. Suspensions in Which the Viscosity Exceeded the Instrument Limit ($5 \times 10^6\text{mPa}\cdot\text{s}$) are Denoted “UM”. Suspensions Below the Specific Viscosity Cut-off Value of 1.1×10^4 Have the Specific Viscosity Value Italicized and Bold.

	Methanol	Ethanol	Isopropanol	Sec-Butanol	Acetone	MEK	Heptane	Toluene	Octanoic Acid	PEG	Water
Rutile	440	150	65	33	66000	11000	UM	UM	33	3.0	0.24
Anatase	830	390	320	220	UM	UM	UM	UM	140	9.9	0.19
Vitreous Silica	0.58	0.29	0.24	0.17	820	4.1	280	110	7.4	0.03	0.21
Quartz	40.	4.3	2.0	3.0	810	220	1100	210	5.2	0.48	1.4
CuO	0.36	0.29	0.32	0.19	90.	10.	48	24	0.16	0.16	0.87
Cu ₂ O	0.79	0.33	0.09	0.13	0.98	0.82	0.27	1.3	240	2.6	UM
Cu	40.	6.5	10.	5.8	2900	74	35000	1400	UM	0.78	1200
Co ₃ O ₄	7.5	13	8.2	3.7	3700	620	1700	190	2.1	0.45	52
Co	280	230	110	41	4900	410	470	370	25	3.8	1400
A-AC	160	88	31	9.5	5500	760	310	740	37	0.48	140
A-HPA	110	57	17	11	2700	680	790	890	24	0.54	150
A-AKP	430	190	86	63	3900	1700	1100	530	33	2.0	380

Table XVII shows that most suspensions tested can be described as unstable as the viscosity cut-off for stability is exceeded (1.1×10^4). Table XVII demonstrates that all suspending mediums produced at least one stable suspension. It is observed that suspensions prepared with PEG had the highest number of stable suspensions.

6.2 *Determination of Stability Mechanism*

It has been demonstrated that steric effects become significant when molecules in the suspension have a chain length which exceeds or equals that of six carbon atoms (i.e. hexane) and becomes the primary mechanism for molecules with a chain length greater than 11 carbon atoms (i.e. undecane).^{7,8} The PEG (average molecular weight of 200g/mol), octanoic acid, and heptane mediums tested exceed the determined critical chain length at which steric effects begin to develop and therefore cannot be considered as purely electrostatic in nature. Even though, the chain length of octanoic acid and heptane result in significant steric effects the primary mechanism is still electrostatic. The chain length of PEG exceeds that of undecane resulting in the primary mechanism for PEG to be steric.

Toluene was not included in the group of mediums in which steric effects become significant because it is an aromatic compound. Since it is aromatic, the molecule is shorter than the aliphatic analogue (heptane) and therefore does not exceed the predicted critical molecule length.

A new technique to determine the stabilizing mechanism is proposed. The dispersion mechanism can be determined by comparing the shear thinning exponent to the specific viscosity of the suspension at a shear rate of 1.0s^{-1} . Figure 16 demonstrates that within 95% confidence, all suspension mediums with the exception of poly(ethylene glycol), octanoic acid, and heptane follow a trend. Therefore it is hypothesized that the significant dispersion mechanism for the mediums within the 95% confidence band of the trend line is an electrostatic mechanism. Mediums that fall outside the defined electrostatic band include other significant forces that are not electrostatic in nature. It is known from previous studies that PEG, heptane, and octanoic acid do not cause stabilization from solely an electrostatic mechanism, but that other mechanisms are present.^{7,8}

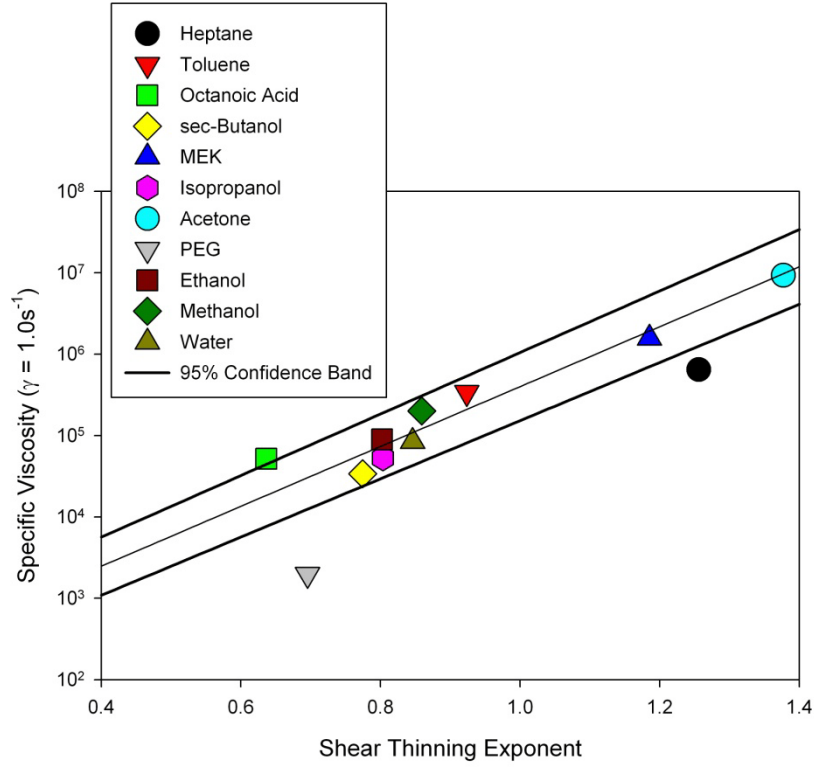


Figure 16. Demonstration that shear thinning exponent and specific viscosity is a function of suspending medium.

Using regression analysis, the equation of the best fit line in Figure 16 is:

$$y = 83.9 \exp(8.47x) \quad (103)$$

With the upper and lower confidence bands having respective equations of:

$$y = 173 \exp(8.70x) \quad (104)$$

$$y = 40.5 \exp(8.23x) \quad (105)$$

Figure 16 demonstrates that toluene does not demonstrate any significant forces caused by stabilization mechanisms other than electrostatic which was predicted by other theories. Heptane and octanoic acid are found just outside the electrostatic band demonstrating that forces from other stabilization mechanisms are significant. Since these points are found just outside the electrostatic band it demonstrates that, although significant, the non-electrostatic effects are not the primary mechanism. PEG is found the farthest outside the electrostatic band as predicted since the chain length exceeds undecane. For PEG the primary mechanism for dispersion is not electrostatic. Figure 16 depicts the primary mechanism for dispersion in water to be an electrostatic mechanism with no significant effects from other mechanisms; however, water is on the border of the electrostatic band demonstrating that other forces do exist albeit negligible. This is most likely due to the hydrogen bonds formed in water.

7.0 Conclusions

The suspension medium which caused the most types of particles to be stabilized was poly(ethylene glycol). Acetone, heptane, and toluene resulted in only one suspension in which the specific viscosity was below the stability cut-off.

The suspension stabilization mechanism can be determined by viscosity measurements. It was shown that by comparison of the shear thinning exponent with the specific viscosity at a shear rate of 1.0s^{-1} a trend develops for suspensions in which the only significant dispersion mechanism is an electrostatic mechanism. When other stabilization mechanisms, such as electrosteric or steric mechanisms, are no longer negligible the parameters of the suspension no longer follow the trend line. It was determined through the master curve that the primary dispersion mechanism of methanol, ethanol, isopropanol, sec-butanol, acetone, 2-butanone, toluene, and water is an electrostatic mechanism. The primary dispersion mechanism of heptane and octanoic acid was also determined to be an electrostatic mechanism; however, because the points did not fall within the 95% confidence interval of the trend line it was determined that other dispersions mechanisms, although not the primary mechanism, are significant and do affect particle interactions. Poly(ethylene glycol) was determined to have a primary dispersion mechanism other than an electrostatic mechanism based upon the master curve. The master curve for dispersion developed is in agreement with the literature and allows for the determination of the applicability of DLVO theory for a given suspension. Therefore DLVO theory would not be applicable for suspensions using heptane, octanoic acid, and poly(ethylene glycol).

8.0 References

1. B.R. Sundlof, "Aqueous Processing of Alumina and Phase Behavior of Polymeric Additives"; Ph.D. Thesis. Alfred University, Alfred, NY, 1999.
2. H.A. Barnes, J.F. Hutton, and K. Walters, *An Introduction to Rheology*; p. 199. Elsevier Science, Amsterdam, Netherlands, 1989.
3. B.W. Ninham, "On Progress in Forces since the DLVO Theory," *Adv. Colloid Interface Sci.*, **83** [1-3] 1-17 (1999).
4. F.J. Rubio-Hernandez, "Is DLVO Theory Valid for Non-Aqueous Suspensions?" *J. Non-Equilib. Thermodyn.*, **24** [1] 75-9 (1999).
5. *CRC Handbook of Chemistry and Physics*, 70th ed. Edited by D.R. Lide CRC Press, New York, 1990.
6. W.M. Carty, "Rheology and Plasticity for Ceramic Processing," pp. 29-52 in *Ceramic Transactions*, Vol. 125, *Fundamentals of Refractory Technology*. Edited by J. P. Bennett and J. D. Smith. American Ceramic Society, Westerville, OH, 2001.
7. B.I. Lee and J.P. Rives, "Dispersion of Alumina Powders in Nonaqueous Media," *Colloids Surf.*, **56**, 25-43 (1991).
8. P.D. Calvert, R.R. Lalanandham, M.V. Parish, J. Fox, H. Lee, R.I. Pober, E.S. Tormey, and H.K. Bowen, "Dispersion of Ceramic Particles in Organic Liquids," pp. 579-84 in *Better Ceramics through Chemistry II*. Edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich. Materials Research Society, Pittsburgh, PA, 1986.

V. PAPER #4

1.0 Title

Predicting Electrostatic Stability of Colloidal Suspensions

Keith J. DeCarlo

William M. Carty

2.0 Keywords

DLVO, Non-aqueous, Inorganic, Colloid, Suspension, Dispersion Model

3.0 Abstract

Electrostatic stability for inorganic colloids in organic mediums was predicted using DLVO theory. Hamaker constants and double-layer potentials were calculated and used to determine the total interaction potential of the respective suspensions. 110 suspensions were tested (11 suspension mediums and 10 types of colloidal particles) in order to create a broad experimental matrix and to test for a robust stability model. An algorithm to predict stability was created by using viscosity as a metric for the total interaction potentials calculated by DLVO theory. It was found that electrostatic suspension stability can be predicted using DLVO theory for non-aqueous mediums.

4.0 Introduction

Electrostatic stability of colloids in a suspension is modeled through DLVO theory.¹ Although the predictions set forth were confirmed for water through force balance studies, the results from non-aqueous suspensions were significantly different.²⁻⁴ The suggested inability of DLVO theory to predict stability of non-aqueous suspensions led to the hypothesis that other “non-DLVO” forces were present in these suspensions.

DLVO theory uses a force balance approach to predict stability. When a particle is placed in a suspension, the particle develops a charged double-layer. This development of a charged double-layer occurs in every medium and the magnitude of the charge is commonly measured by ζ -potential. How the charge is developed in non-aqueous mediums, especially those that are

non-polar, is still not completely understood; what is important is that particles in these mediums demonstrate the generation of a double-layer by having a non-zero ζ -potential.⁵⁻⁸ This envelopment of a colloidal particle with charge (the double-layer) causes the net charge on the particle to decay to zero and is the same (sign and magnitude) for similar particles in the suspension. Therefore, since the same charge is developed for similar particles, when the double-layers start to interact with one another, a repulsive potential (V_R) can be calculated.^{1,9-12} According to DLVO theory, in order for the particles to be dispersed (act independently) the developed repulsive force must overcome the intrinsic van der Waals attractive force between the particles.

The development of van der Waals attraction between particles does not require the particles to be in a medium, the force is present in a vacuum.¹³⁻¹⁵ However, the inclusion of an intervening medium between particles will act to modify the potential.¹³ The van der Waals force has its basis in the quantum mechanics of the atoms and molecules through which an attractive potential (V_A) can be calculated.^{4,9-25}

The total interaction potential is realized by the summation of the attractive and repulsive terms (V_A and V_R) as a function of separation distance (all variables are defined at the end of the chapter):^{1,9-12,22}

$$V_T = \sum_{D=2nm}^{20nm} \left[-A_{132} \frac{1}{12\pi D^2} + 2(U_m - U_\infty) \right] \quad (106)$$

The summation in Equation 106 is from 2 to 20 nm because of limitations of the van der Waals potential calculations. At separation distances larger than 20nm, retardation effects become significant causing the Hamaker constant to be a function of separation distance.^{13,15} At separation distances smaller than 2nm, the Hamaker constant will again be dependent on separation distance due to the effect of the wave vector on the permittivity.²⁶

5.0 Experimental

Colloids were evaluated in 12 different suspending mediums. All non-aqueous mediums were designated as anhydrous by the supplier (but this was not verified). The mediums were chosen based on polarity and functional group. Polarity of the mediums was measured by the relative

static permittivities (dielectric constants) and ranged from 1.9 (heptane) to 78.5 (water) at 298K. Functional groups that were studied included alcohols, ketones, carboxylic acids, and glycols, using a variety of aliphatics and aromatics. Poly(ethylene glycol) was the only polymeric medium studied. In order to keep the poly(ethylene glycol) as a liquid at 298K and avoid spontaneous crystallization, 200 molecular weight was used. 2-Butanone and poly(ethylene glycol) will be referred to as MEK and PEG, respectively.

Table XVIII. Characterization of the Suspending Mediums Used. They are Listed in Order of Increasing Relative Static Permittivity.

Suspending Medium	Relative Static Permittivity,		Chemical Class	Functional Group	Structure
	At 298K	$\epsilon_{r,static}$ Reference			
Heptane	1.90	27	Alkane	N/A	Aliphatic
Toluene	2.40	28	N/A	Phenyl	Aromatic
Octanoic Acid	2.50	27	Carboxylic Acid	Carboxyl	Aliphatic
sec-Butanol	15.8	28	Alcohol	Hydroxyl	Aliphatic
2-Butanone	18.2	29	Ketone	Carbonyl	Aliphatic
Isopropanol	18.3	28	Alcohol	Hydroxyl	Aliphatic
Acetone	20.7	28	Ketone	Carbonyl	Aliphatic
Poly(ethylene glycol)	22.1	30	Polymer	Hydroxyl	Aliphatic
Ethanol	24.3	28	Alcohol	Hydroxyl	Aliphatic
Methanol	32.6	28	Alcohol	Hydroxyl	Aliphatic
Water	78.5	28	N/A	N/A	N/A

Colloids were chosen based upon the isoelectric points (IEP) determined by the Parks relationship which correlates the ion size (S) and valence (z) to the IEP (Figure 17).^{31,32}

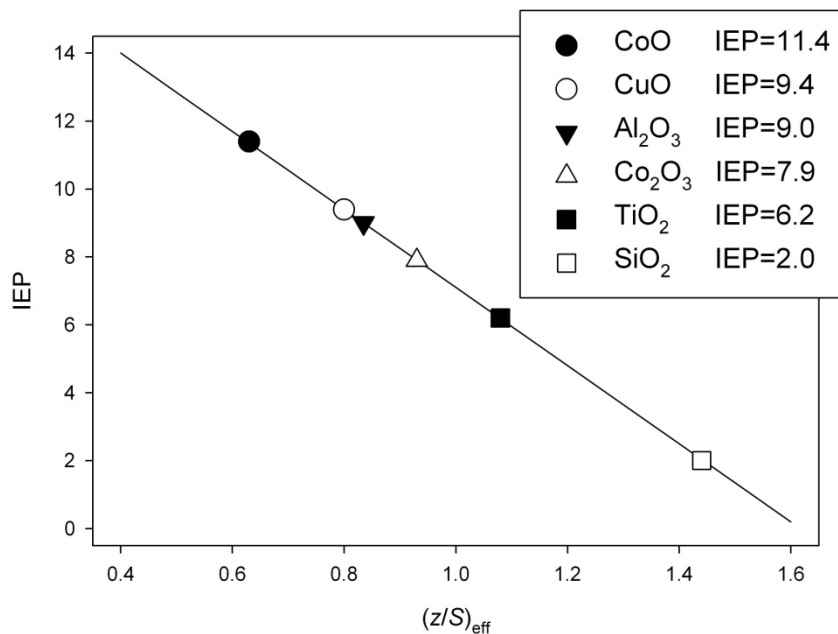


Figure 17. Isoelectric points of some of the colloidal particles tested adapted from Parks.³² The Park's relationship between the IEP and the size and valence of the cation is shown.

The isoelectric point corresponds to the pH at which the shear plane of the colloids have no net charge. The surface of the colloid becomes neutral through a series of equilibrium reactions between the particle surface and the medium.³² At pH values close to the IEP, since the double-layer charge is negligible, attractive forces will dominate the system and cause the colloids to agglomerate. The IEP can only be measured in aqueous suspensions because of the correlation to pH, pH is not a measurable property in non-aqueous mediums and therefore IEP cannot be defined. It is hypothesized however, that since the different particles act differently in water (requiring a distinct equilibrium to form), different particles should also act differently in non-aqueous suspensions. In addition to choosing colloid types based upon their respective IEP, the ionic nature of the bonds and stoichiometry was varied. A range of ionic characters from 0 (covalent bonding) to 2.2 (ionic bonding) was demonstrated within the group of colloids tested. The only non-stoichiometric colloid tested was Co₃O₄ (CoO·Co₂O₃).

Table XIX. Characterization of the Colloids Tested in Order of Increasing Electronegativity Difference

Chemistry	Powder	ID	IEP	Ionic Character
SiO ₂	Quartz	Quartz	2.0	1.7
SiO ₂	Vitreous	Vitreous Silica		
Cu ₂ O		Cu ₂ O	N/A	1.7
CuO		CuO	9.4	1.7
Co ₃ O ₄		Co ₃ O ₄	N/A	1.8
Al ₂ O ₃	Aluchem AC16SG	A-AC	9.0	2.0
Al ₂ O ₃	Ceralox HPA-1.0	A-HPA		
Al ₂ O ₃	Sumitomo AKP30	A-AKP		
TiO ₂	Anatase	Anatase	6.2	2.2
TiO ₂	Rutile	Rutile		

To determine if any chemical interactions between the colloid and medium were occurring, 50ml suspensions of 5vol% solids were prepared. The suspensions were ultrasonicated for 150s and then mixed using a rotary mill for 18 hours. The resulting suspensions were then dried in the fume hood (average temperature of 291K) for one week. The resulting powder was analyzed via Helium pycnometry to determine if a significant change in density occurred. Observation of a change in density of the powder would indicate that chemical reactions had taken place sufficient enough to change the bulk chemistry of the powder. Suspensions prepared using poly(ethylene glycol) or octanoic acid as the medium were not tested because the vapor pressure of the respective mediums were extremely low at 291K requiring higher temperatures to evaporate. Increasing the temperature may cause sintering or a chemical reaction to occur which was not desirable for the experiment.

The parameters concerning the viscosity experiments are described in a previous paper.

6.0 Results and Discussion

6.1 Repulsive Potential

From the ζ -potential measurements, the repulsive potential between particles due to double-layer overlap can be calculated. All corrected ζ -potential measurements are found in Table XX. The ζ -potential acts as a scalar factor; however, the shape of the curves always is similar and is dictated by the Debye-length parameter which corresponds to the thickness of the double-layer.

The Debye-length is inversely proportional to the double-layer thickness and is a function of the static permittivity of the suspension medium. Therefore as polarity of the medium increases, the larger the associated double-layer. The larger the double-layer, the less of a charge decay from the particle surface towards the bulk. Since the decay of charge is much less in polar mediums, the double-layers of colloids will begin to interact at larger separation distances compared to when a non-polar medium is used. The effect of medium polarity can be observed in Figure 18.

Table XX. Corrected ζ -potential Measurements (mV) of the Colloids in the Various Mediums at 298K

	Water	Methanol	Ethanol	Isopropanol	Acetone	MEK	PEG	Sec-Butanol	Heptane	Toluene	Octanoic Acid
Rutile	-38.6	-2.00	-32.4	-29.3	-41.2	-47.2	-33.1	3.70	56.2	13.7	150
Anatase	-42.2	-40.0	-26.0	-0.900	-41.6	-73.1	-16.2	15.2	113	0.000	84.3
Quartz	-36.4	-5.00	-38.0	-28.0	-58.9	-62.0	0.000	-10.6	23.3	41.4	0.000
Vitreous Silica	-33.1	-40.9	-25.3	-33.4	-69.3	-56.2	-50.7	-10.1	0.000	0.000	0.000
CuO	-26.5	-28.9	-51.9	-34.8	-40.9	-29.5	-19.6	18.3	0.00	-8.60	18.0
Cu ₂ O	-29.5	-2.70	-20.4	-22.0	-26.1	-16.5	179	33.3	3.80	126	54.0
Cu	-42.6	14.9	28.9	-48.3	-38.5	-28.3	-15.3	21.3	-1.60	0.000	33.8
Co ₃ O ₄	-48.0	-15.0	-4.7.0	-55.8	7.30	-31.5	0.000	25.7	-9.70	-37.7	-36.9
Co	13.8	-25.9	-30.1	-26.7	-24.9	-65.8	68.0	14.9	30.6	92.3	29.0
A-AC	26.5	-8.00	-11.2	-18.5	-54.2	-36.7	-23.6	28.1	71.5	0.000	0.000
A-HPA	17.4	-15.4	-12.1	-22.3	-75.3	-40.2	-75.9	13.0	107	-40.4	0.000
A-AKP	27.2	-9.10	-10.6	-13.4	-69.1	-60.9	-18.4	35.6	15.0	-14.0	37.0

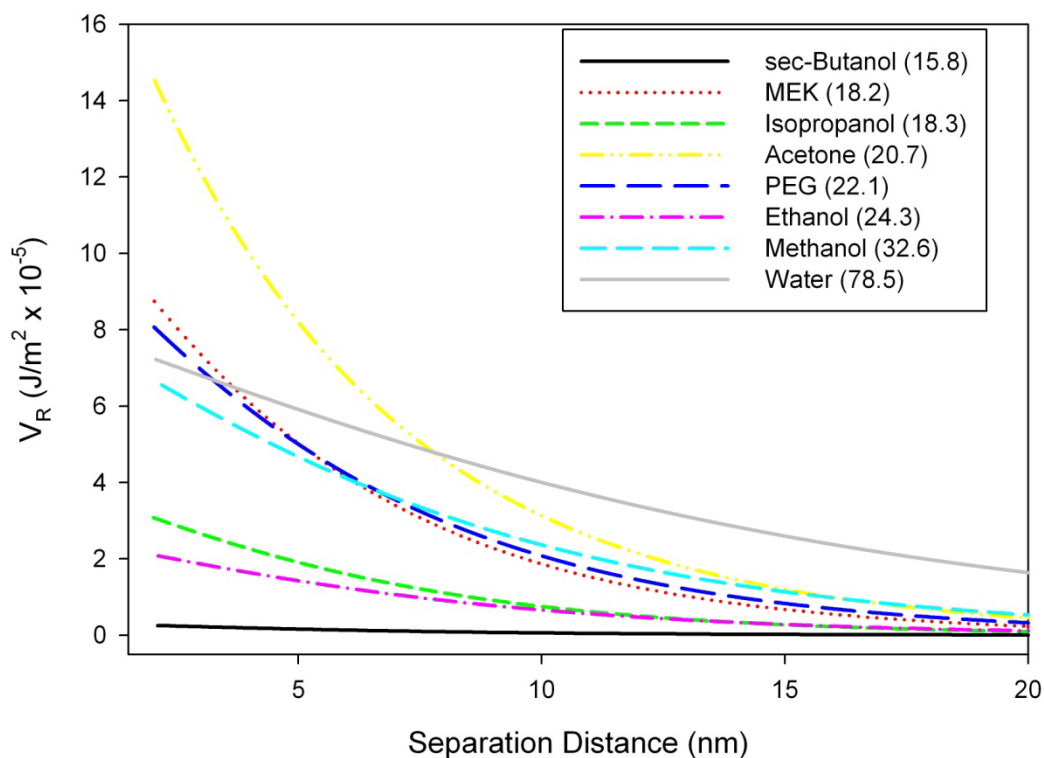


Figure 18. Repulsive potential generated in vitreous silica as a function of separation distance for different suspending mediums. The static dielectric constant of each medium is noted in the parentheses.

6.2 Attractive Potential

To determine the total interaction potential between colloidal particles the attractive force must also be calculated. The attractive force between colloidal particles in a medium is dictated by the van der Waals forces which is commonly described by the Hamaker constant. The Hamaker constant is a material specific term and therefore only a function of the colloid and the medium. The non-retarded Hamaker constant between similar colloids in each medium is listed in Table XXI. It is observed that the Hamaker constant varies greatly with respect to colloid type, with a range over two orders of magnitude. However with respect to suspending medium, the variability of the Hamaker constant is reduced.

Table XXI. Calculated Non-retarded Hamaker Constants ($\times 10^{-20}\text{J}$) at 298K Between Similar Colloids in Each Medium

	Vitreous Silica	Quartz	CuO	Cu ₂ O	Al ₂ O ₃	Anatase	Rutile	Co ₃ O ₄
Water	0.46	1.0	3.5	3.8	3.8	4.0	5.4	33
Methanol	0.81	1.5	2.7	2.6	4.5	3.2	5.2	35
Ethanol	0.51	1.1	2.8	2.9	4.0	3.4	5.2	34
Isopropanol	0.50	1.2	3.0	3.0	4.3	3.5	5.5	35
sec-Butanol	0.59	1.3	2.6	2.5	4.4	3.2	5.2	36
Acetone	0.62	1.4	3.4	3.4	4.7	4.0	6.1	36
MEK	1.0	1.4	1.9	2.0	3.7	2.2	3.8	33
Heptane	0.29	1.0	3.5	3.4	4.1	4.1	5.7	34
Toluene	0.38	1.0	2.6	2.7	4.1	3.1	4.9	35
Octanoic Acid	0.10	0.6	3.1	3.2	3.3	3.6	5.0	33
PEG	1.2	1.2	1.6	2.1	2.6	1.7	2.6	30

Attractive potential as a function of particle separation distance curves have the same shape, unlike the repulsive potential curves. The Hamaker constant is a scalar quantity and thus dictates only the magnitude of the potential (Figure 19).

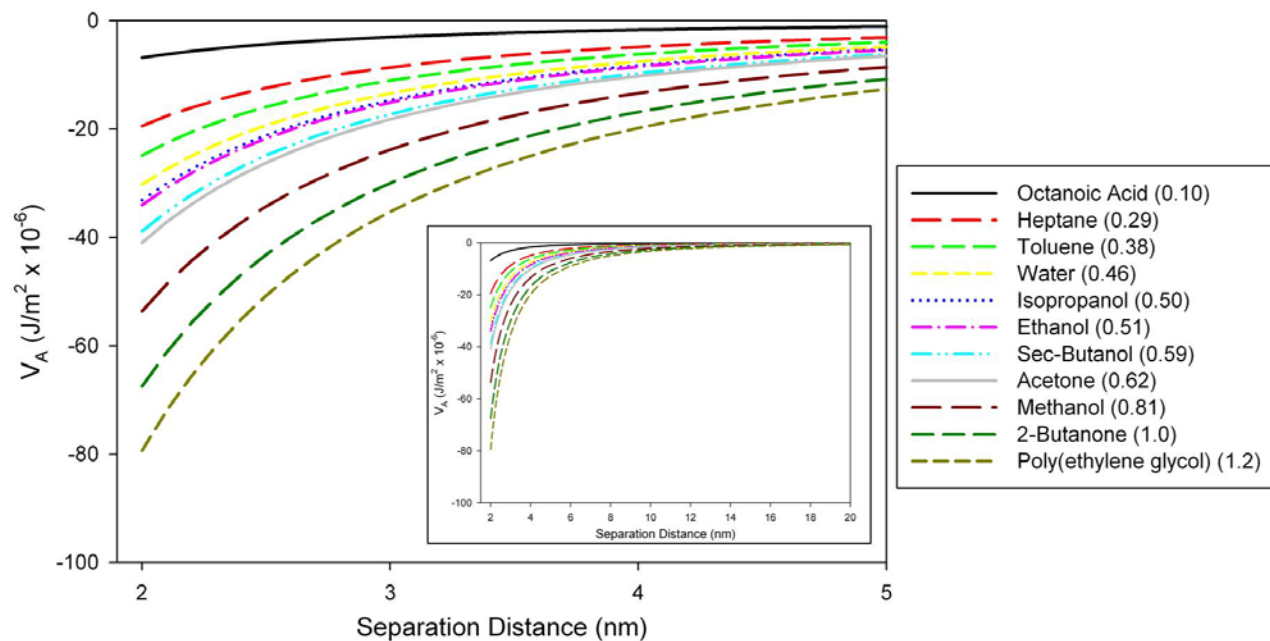


Figure 19. Total van der Waals attractive potential as a function of separation distance and calculated non-retarded Hamaker constants ($\times 10^{-20} \text{ J}$) for vitreous silica in parentheses next to the identified medium.

6.3 Total Interaction Potential

Total potential interaction energy curves were calculated for each medium-colloid combination by summation of the repulsive and attractive potentials (Equation 106, Figure 20). Figure 20 demonstrates the types of curves generated for vitreous silica in selected mediums.

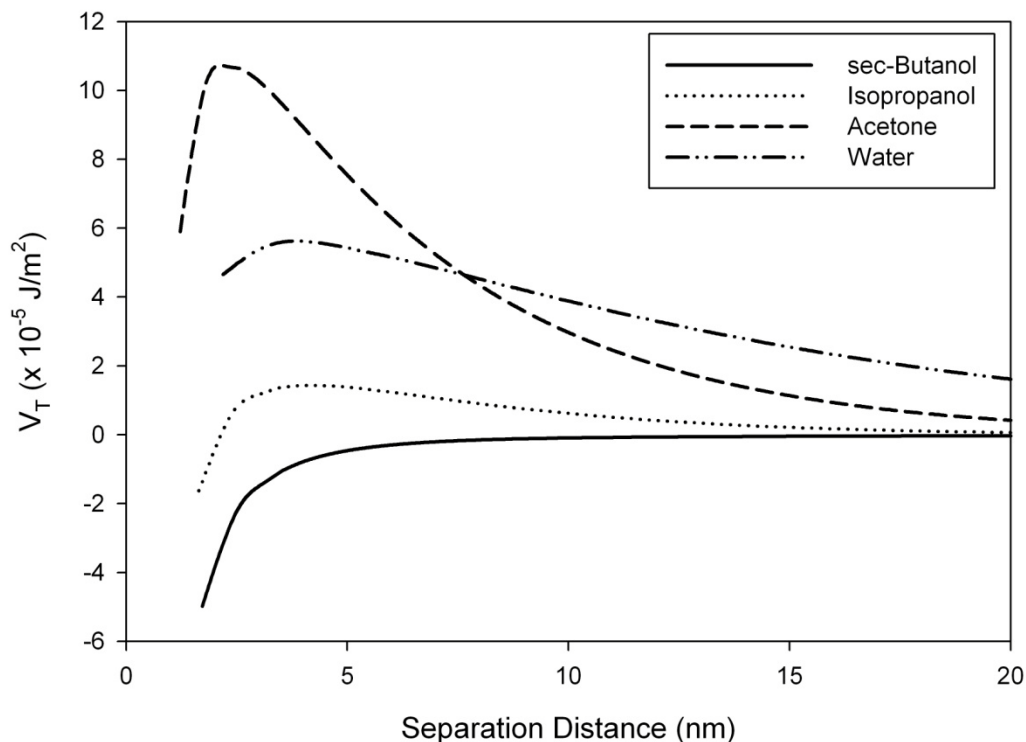


Figure 20. Total interaction potential curves of vitreous silica as a function of separation distance for the selected mediums.

Water and acetone generate the largest repulsive forces in vitreous silica. Isopropanol also causes a repulsive force between particles to develop; however, the generated potential is much smaller than those generated in acetone and water.

It is possible for the colloids to overcome the repulsive potential and move into the attractive potential region through Brownian motion. The forces exerted on the colloids caused by Brownian motion may be large enough to overcome the repulsive potential and cause the colloids to move close enough together resulting in agglomeration. Suspensions demonstrating this type of behavior will be dependent on temperature since Brownian motion is a thermal phenomenon. The suspension using sec-butanol as the medium shows no repulsive forces developing; therefore, the colloids will move into the lowest energy state at a small separation distance (approximately 2nm) resulting in agglomeration. In this case there is no potential barrier the colloids need to overcome though the Brownian motion, agglomeration will occur regardless of temperature. Of the 110 suspensions tested, 70 demonstrated only an attractive

potential between particles (Figure 20, sec-Butanol). Therefore the majority of suspensions were predicted to be unstable (Table XXII).

Table XXII. Suspensions Which Were Predicted to be Unstable via Total Interaction Potential Calculations are Labeled “US” (for unstable) Whereas the Suspensions Which Demonstrated Repulsive Forces Between Particles at any Separation Distance are Labeled “SU” (for stability unknown)

	Methanol	Ethanol	Isopropanol	Sec-Butanol	Acetone	MEK	Heptane	Toluene	Octanoic Acid	PEG	Water
Rutile	US	US	US	US	US	SU	US	US	US	SU	SU
Anatase	SU	SU	US	US	SU	SU	US	US	US	US	SU
Vitreous Silica	SU	SU	SU	US	SU	SU	US	US	US	SU	SU
Quartz	US	SU	SU	US	SU	SU	US	US	US	US	SU
CuO	SU	SU	SU	US	SU	SU	US	US	US	US	SU
Cu ₂ O	US	US	US	SU	US	US	US	US	US	SU	SU
Co ₃ O ₄	US	US	US	US	US	US	US	US	US	US	SU
A-AC	US	US	US	US	SU	US	US	US	US	US	SU
A-HPA	US	US	US	US	SU	US	US	US	US	SU	US
A-AKP	US	US	US	US	SU	SU	US	US	US	US	SU

Table XXII shows that the three non-polar mediums (heptane, toluene, and octanoic acid) are predicted to cause agglomeration to occur in every type of colloid tested. Water is inconclusive for all colloids, except for A-HPA, resulting in the hypothesis that water may be the best medium to induce dispersion without the need to incorporate an additive. It is known that this prediction, for colloids to be dispersed in water with no additives, is invalid. The reason for this prediction is due to the method for measuring ζ -potential. ζ -potential measurements were completed using very low solids loading (approximately 0.01 vol%) to reduce the interactions between particles; however, at these solids loadings the intrinsic COO^- ions will affect the surface reactions. At larger solids loadings, such as those used in the viscosity measurements, the COO^- ions are at a relatively low concentration compared to the area of particle surface available that the effect becomes negligible.

In addition to removing water from the experimental matrix, it is proposed that suspensions prepared with PEG, heptane, and octanoic acid also be removed. Predictions set forth from DLVO theory only include suspensions that are electrostatically stabilized. Suspensions which include other stabilization mechanisms will not follow the predictions made by DLVO theory. It has been demonstrated that PEG, heptane, and octanoic acid introduce steric effects into the suspension resulting in other non-electrostatic forces to develop.^{33,34}

It is also important to discern what effects, if any, the mediums have on the particles. If a medium causes the bulk particle to dissolve or cause a chemical reaction to occur, the value of the total interaction potential may not follow the DLVO prediction because of the chemical change of the particle or the suspension medium. Dissolution (where atoms in the molecules of the colloid become separated), solvation (in which the molecules of the colloid are complexed by the medium), or oxidation/reduction reactions of the colloids in the mediums (oxidation or surface hydration) may have an effect on measured viscosities and ζ -potentials therefore making it important to identify potential interactions.

All measured densities of the treated powders fell within a 5% difference with the original measured density indicating that there were no significant colloid-medium interactions occurring. However, Cu_2O presented a problem. It was observed that with a higher solids loadings (20 vol%) the Cu_2O demonstrated solvation effects noted when completing the viscosity measurements leading to the colloid-medium interaction experiment described. Such observations included adsorption or solvation of the medium with the Cu_2O colloids resulting in no liquid phase present and discoloration of the suspension to a light green color. Therefore Cu_2O was considered interacting with the mediums and therefore removed from the experimental

matrix. No other such observations were made when conducting the viscosity experiments with the other suspensions.

The experimental matrix has been reduced to exclude mediums that cause dispersion mechanisms other than electrostatic to develop and colloids that interact with the selected mediums. The resulting matrix includes seven mediums (excluding poly(ethylene glycol), octanoic acid, heptane, and water) and 12 types of colloids (excluding Cu_2O). For each of the suspensions the thermal boundary and the separation of the secondary minimum were recorded if they were present. No thermal boundaries were calculated for the suspensions deemed to be unstable (Figure 20, sec-butanol). A table was generated to discern which of the suspensions exhibited a thermal boundary and which did not (Table XXIII).

Table XXIII. Determination of the Thermal Boundary (in $\text{J/m}^2 \times 10^{-6}$) of the Suspensions in the Reduced Experimental Matrix. Suspensions Labeled N/A did not Show a Thermal Boundary.

	Methanol	Ethanol	Isopropanol	Sec-Butanol	Acetone	MEK	Toluene
A-AKP	N/A	N/A	N/A	N/A	34	21	N/A
A-HPA	N/A	N/A	N/A	N/A	45	N/A	N/A
A-AC	N/A	N/A	N/A	N/A	13	N/A	N/A
Co_3O_4	N/A	N/A	N/A	N/A	N/A	N/A	N/A
CuO	5.9	28	1.2	N/A	5.3	1.6	N/A
Quartz	N/A	20.	3.3	N/A	110	45	N/A
Vitreous Silica	39	8.9	14	N/A	110	45	N/A
Anatase	0.03	N/A	N/A	N/A	3.9	61	N/A
Rutile	N/A	N/A	N/A	N/A	N/A	5.7	N/A

Therefore according to Table XXIII, a large number of suspensions were calculated to be unstable. All suspensions using sec-butanol and toluene as the medium are predicted to be unstable. At this point it is still unclear as to what the magnitude of the thermal boundary is required to cause the colloids to move into the secondary minimum rather than the primary minimum. A thermal boundary which is too small will be overcome by colloids due to the intrinsic thermal energy and therefore cause agglomeration to occur since the colloids would then reside at the primary minimum. If the thermal boundary is larger than the intrinsic thermal energy of the colloids, the colloids will move to the secondary minimum and either act independently or as a weakly flocculated suspension depending on the separation distance at the secondary minimum.

To determine the intrinsic thermal energy of the colloids at 298K, the calculated thermal boundaries were compared to the viscosity measurements. Specific viscosities above the cut-off value (1.1×10^4) were deemed unstable and therefore if a suspension showed a thermal boundary and a specific viscosity above the reference value, the intrinsic thermal energy of the colloids was enough to overcome the thermal boundary (Figure 21).

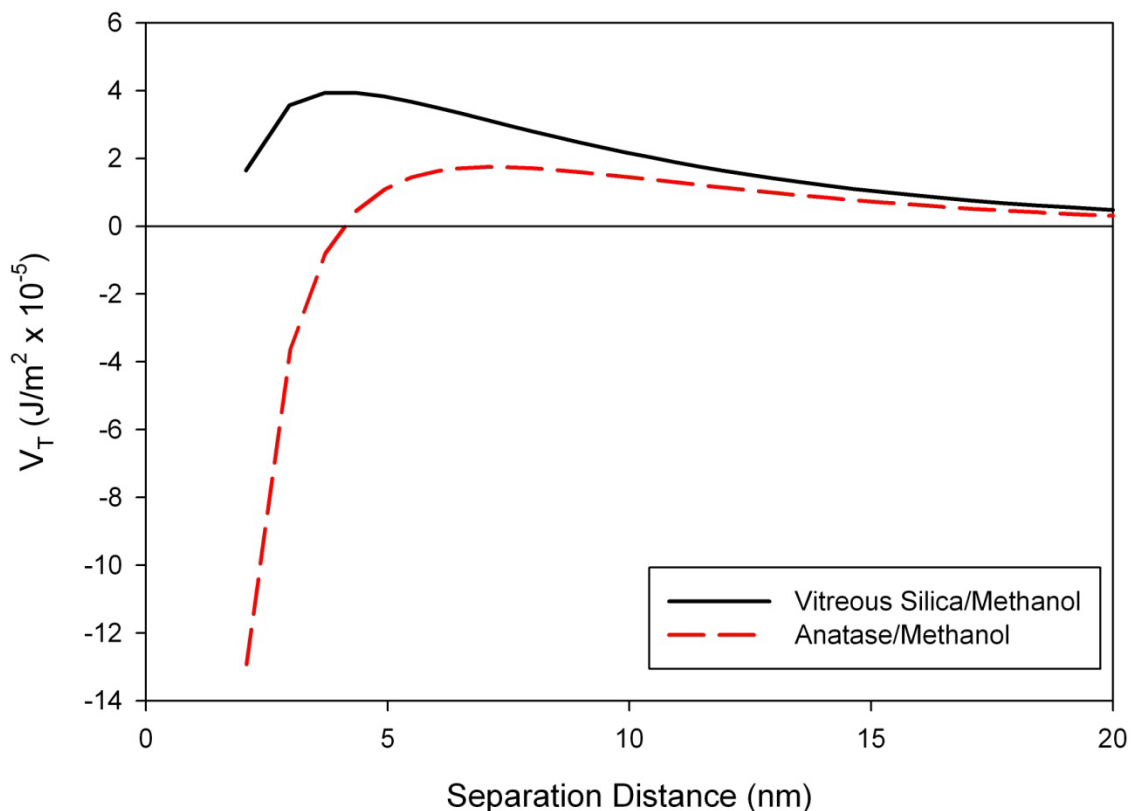


Figure 21. Vitreous silica and anatase suspended in methanol demonstrating the smaller thermal boundary calculated in anatase was overcome by the particles causing them to move into the primary minimum resulting in an unstable suspension (high viscosity). The thermal boundary present for vitreous silica was large enough to cause the suspended colloids to move to the secondary minimum.

Comparison of the specific viscosities of the suspensions and Table XXIII led to the conclusion that the intrinsic thermal energy of the colloids at 298K is $2.0 \times 10^{-6} (\pm 1.9 \times 10^{-6}) \text{ J/m}^2$. Therefore if the thermal boundary predicted by DLVO theory is less than approximately $2.0 \times 10^{-6} \text{ J/m}^2$, the intrinsic thermal energy of the colloids is large enough to overcome the barrier resulting in agglomeration at the primary minimum. If the thermal boundary energy is larger than $2.0 \times 10^{-6} \text{ J/m}^2$ the colloids will reside at the secondary minimum.

When colloidal particles adopt a separation distance equivalent to the secondary minimum, the suspension can either be weakly flocculated or stable depending upon that separation distance and the magnitude of the van der Waals attraction or the depth of the secondary minimum. A

weakly flocculated suspension can be characterized rheologically as a suspension with a large shear thinning exponent, (i.e. $n > 1.0$).

Table XXIV shows that suspensions made with acetone and 2-butanone demonstrate a weakly flocculated case whereas the other suspensions do not and are considered stable. This effect has been related to the equilibrium separation distance at the secondary minimum (Table XXV).

Table XXIV. Shear Thinning Exponents, n , of the Experimental Matrix in Which the Stability was Deemed Unknown. Suspensions Labeled N/A were Deemed Unstable.

	Methanol	Ethanol	Isopropanol	Acetone	MEK
A-AKP	N/A	N/A	N/A	1.2	1.4
A-HPA	N/A	N/A	N/A	1.5	N/A
A-AC	N/A	N/A	N/A	1.5	N/A
CuO	0.6	0.9	0.6	1.6	1.5
Quartz	N/A	0.6	0.8	1.3	1.1
Vitreous Silica	0.8	0.7	0.8	1.7	0.8
Anatase	0.9	N/A	N/A	N/A	N/A
Rutile	N/A	N/A	N/A	N/A	1.5

Table XXV. Equilibrium Separation Distance (in nm) at the Secondary Minimum for Suspensions in Which the Stability was Unknown. Suspensions Labeled N/A were Deemed Unstable.

	Methanol	Ethanol	Isopropanol	Acetone	MEK
A-AKP	N/A	N/A	N/A	33.3	28.8
A-HPA	N/A	N/A	N/A	33.0	N/A
A-AC	N/A	N/A	N/A	28.7	N/A
CuO	39.6	36.7	21.9	27.2	23.1
Quartz	N/A	41.4	27.6	44.5	35.2
Vitreous Silica	56.5	41.7	36.0	44.2	35.4
Anatase	42.9	N/A	N/A	25.6	34.9
Rutile	N/A	N/A	N/A	N/A	25.4

Comparison of Table XXIV and Table XXV leads to the hypothesis that the minimum separation distance for stability at the secondary minimum is 40 ± 5 nm. If the equilibrium separation distance is less than 40 ± 5 nm, the suspension will be weakly flocculated and characterized by a

shear thinning exponent greater than 1.0. These findings have been consolidated into a flow chart to determine stability (Figure 22). The results of application of Figure 22 to the suspensions tested are found in Table XXVI.

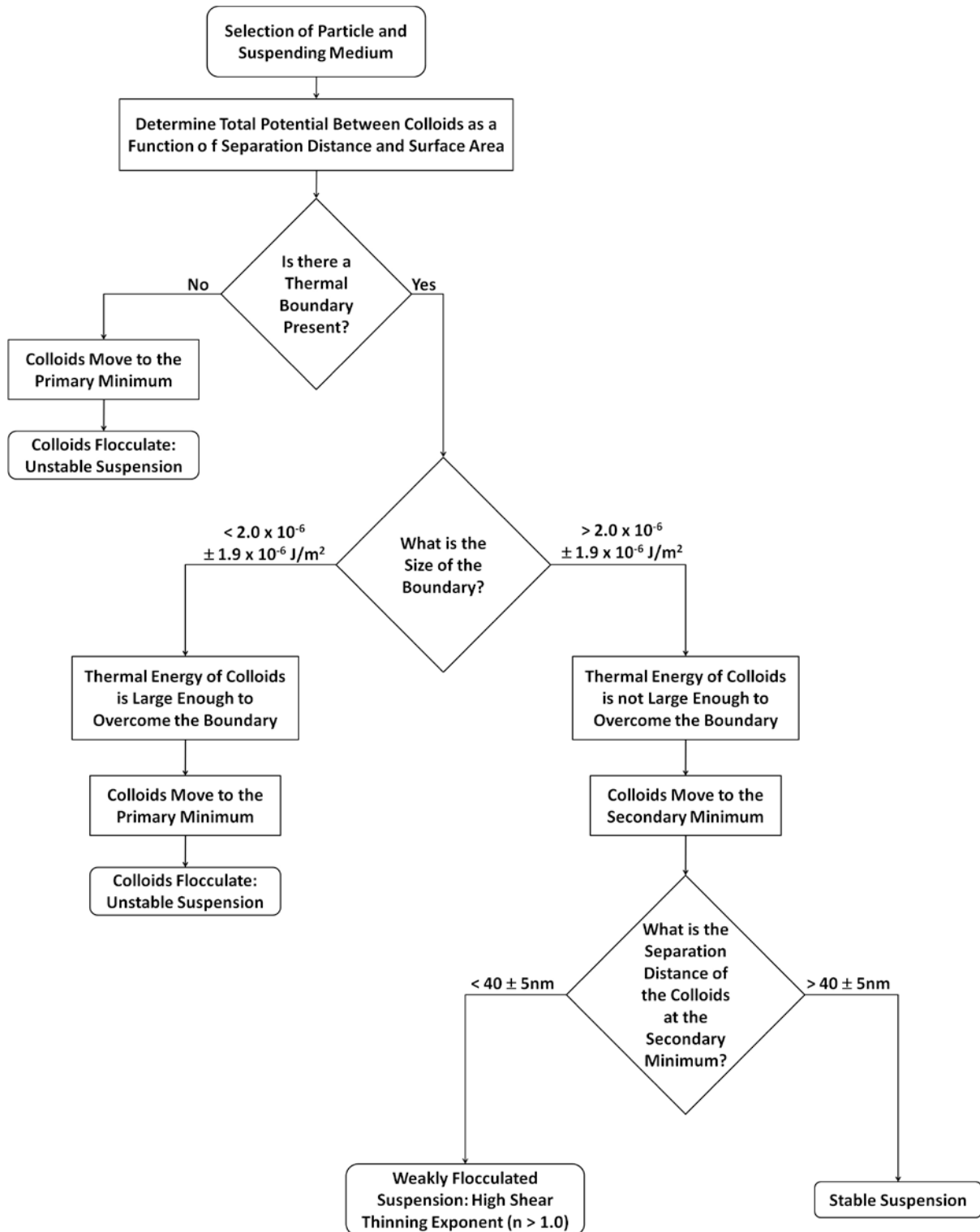


Figure 22. Flow chart depicting the requirements to discern if a suspension will be stable or not using DLVO theory.

Table XXVI. Results Using the Flow Chart in Figure 22 to Discern the Stability of the Suspension. US – Unstable, **S** – Stable, and **WF** – Weakly Flocculated.

	Methanol	Ethanol	Isopropanol	Sec-Butanol	Acetone	MEK	Toluene
A-AKP	US	US	US	US	WF	WF	US
A-HPA	US	US	US	US	WF	US	US
A-AC	US	US	US	US	WF	US	US
Co ₃ O ₄	US	US	US	US	US	US	US
CuO	S	S	WF	US	S	S	US
Quartz	US	S	WF	US	WF	WF	US
Vitreous Silica	S	S	S	US	WF	S	US
Anatase	US	US	US	US	US	WF	US
Rutile	US	US	US	US	US	WF	US

There exists four types of outliers that do not follow the flow chart in Figure 22. The first type occurs when the measured viscosity is within the stable region; however, the DLVO prediction is that the colloids will move to the primary minimum and be strongly flocculated. This is observed when using sec-butanol as the suspending medium and CuO, Co₃O₄, vitreous silica, quartz, A-HPA, and A-AC as the colloids. It is unclear as to why the viscosities measured are within the stable region; however, it is hypothesized that since sec-butanol wets the viscometer plates, error was induced from the flow behavior.

The second type of outlier is observed with suspensions of isopropanol and CuO or quartz. Here the predicted behavior is that the suspensions would be weakly flocculated; however, this is not supported by the shear thinning exponent values (0.6 and 0.8 respectively). This is most likely caused by the suspension viscosity moving out of the measureable range of the viscometer at the higher shear rates.

The third type of outlier exists in the suspension of 2-butanone and anatase. The viscosity of the respective suspension was unmeasurable suggesting that the colloids have moved to the primary minimum; however, the DLVO theory predicts that the colloids are at the secondary minimum and therefore should be weakly flocculated. It is possible that a large shear thinning exponent ($n > 1.0$) exists for this suspension; however, since the viscosity was extremely high and out of the measurable regime of the instrument used this could not be verified.

The fourth type of outlier is observed in only Co_3O_4 suspensions made using methanol and isopropanol. In this case the measured viscosity is below the stability cut-off; however, the DLVO theory predicts that all Co_3O_4 suspensions will be unstable. It is hypothesized that Co_3O_4 being non-stoichiometric may have an effect in these mediums.

7.0 Conclusions

DLVO theory was used to predict the stability of colloids suspended in non-aqueous mediums. This required the calculation of the intrinsic van der Waals force, commonly described by the Hamaker constant, and the ion generated repulsive force. Van der Waals forces were calculated via the macroscopic (Lifshitz) method using the Ninham-Parsegian dielectric representation. It was found that the medium did not have as large an effect as the colloid type did. The two silica types, quartz (crystalline) and vitreous (amorphous), had the lowest calculated van der Waals forces whereas the Co_3O_4 colloids demonstrated the largest van der Waals forces. In order to overcome the intrinsic attractive force developed by the colloids and the subsequent agglomeration due to this force, a repulsive force is required and developed by generation of a double-layer. Since only similar colloids were used in suspensions, the charge on the double-layer of all colloids in the respective suspension would be the same and the interaction of two similarly charged double-layers would result in a repulsive force. The key to producing a stable or dispersed suspension is to generate a double-layer in which the magnitude to the charge is large enough to overcome the attractive van der Waals forces. The charge (magnitude and sign) of the double-layer was measured via the ζ -potential for each of the suspensions tested.

The total interaction potential between two colloids in the respective medium was calculated by the summation of the attractive force and the repulsive force. The attractive potential is negative in sign, demonstrating a low energy state and therefore desirable, where the repulsive potential is positive signifying an increased energy state for the colloids. Therefore colloids will always attempt to agglomerate; however, by generating a repulsive potential the total interaction potential can result in acquiring an energy barrier from which the colloids will have to overcome in order to agglomerate or completely exceed the magnitude of the attractive potential causing the lowest energy state to be at a large separation distance. Total interaction as a function of separation distance was determined for each suspension in the experimental matrix.

It is important to be aware that DLVO only looks to predict electrostatic stabilization mechanisms; therefore, if another stabilization method is employed the DLVO model will not be

applicable. The hypothesized “non-DLVO” forces are most likely an artifact of a different stabilization technique. Based upon the assumptions of the DLVO theory the original experimental matrix was modified to remove suspensions which did have other mechanisms operating. To do this a master curve was defined which correlated specific viscosity at a shear rate of 1.0s^{-1} to the shear thinning exponent. Suspension mediums which did not follow the defined trend include heptane, octanoic acid, and poly(ethylene glycol) and were therefore removed from the experimental matrix. The generated master curve is in good correlation to the current literature which shows that steric effects start to arise when the chain length exceeds 6 carbon atoms.³³

In addition to DLVO calculations, viscosity was measured as a way to determine suspension stability (low viscosity values correlate to a stable suspension). It was found that colloids have a thermal energy of $2.0 \times 10^6 \pm 1.9 \times 10^6 \text{ J/m}^2$. Therefore if the energy barrier formed from the interaction of the attractive and repulsive potentials is larger than the thermal energy of the colloids, the colloids will not overcome the barrier and move into the secondary minimum. If the energy of the barrier is less than that of the thermal energy of the colloids the colloids will move into the primary minimum and agglomerate. If the colloids are in the secondary minimum the suspension can be either weakly flocculated, if the separation distance between colloids at the secondary minimum is less than $40 \pm 5\text{nm}$, or stable, if the separation distance between colloids at the secondary minimum is greater than $40 \pm 5\text{nm}$. Based upon the revised experimental matrix a flow chart (Figure 22) was developed to ascertain if a suspension is predicted to be stable. The developed flow chart demonstrated good correlation with viscosity measurements.

8.0 List of Variables

A_{132} – Hamaker constant between two different colloids of material type 1 and 2 separated by a dielectric medium (3)

D – Total separation distance

T – Temperature

U_m – Free energy at the mid-point plane between interacting particles

U_∞ – Free energy of the bulk suspension

V_T – Total interaction potential

$\epsilon_{r,static}$ – Relative static permittivity (Dielectric constant)

η – Viscosity at 298K

ζ – ζ -potential

9.0 References

1. E.J.W. Verwey and J.T.G. Overbeek, *Theory of the Stability of Lyophobic Colloids*; p. 205. Elsevier, New York, 1948.
2. F.J. Rubio-Hernandez, "Is DLVO Theory Valid for Non-Aqueous Suspensions?" *J. Non-Equilib. Thermodyn.*, **24** [1] 75-9 (1999).
3. B.W. Ninham, "On Progress in Forces since the DLVO Theory," *Adv. Colloid Interface Sci.*, **83** [1-3] 1-17 (1999).
4. D. Tabor and R.H.S. Winterton, "Direct Measurement of Normal and Retarded van der Waals Forces," *Proc. R. Soc. London, A*, **312** [1511] 435-50 (1969).
5. R. Xu, C. Wu, and H. Xu, "Particle Size and Zeta Potential of Carbon Black in Liquid Media," *Carbon*, **45** [14] 2806-9 (2007).
6. R.E. Johnson, Jr. and W.H. Morrison, Jr., "Ceramic Powder Dispersion in Nonaqueous Systems," pp. 323-48 in *Advances in Ceramics*, Vol. 21, *Ceramic Powder Science*. Edited by G. L. Messing, J. W. McCauley, and K. S. Mazdidasni. American Ceramic Society, Westerville, OH, 1987.
7. F.M. Fowkes, "Dispersions of Ceramic Powders in Organic Media," pp. 411-21 in *Advances in Ceramics*, Vol. 21, *Ceramic Powder Science*. Edited by G. L. Messing, J. W. McCauley, and K. S. Mazdidasni. American Ceramic Society, Westerville, OH, 1987.
8. R.J. Pugh, "Dispersion and Stability of Ceramic Powders in Liquids," pp. 127-92 in *Surfactant Science Series*, Vol. 51, *Surface and Colloid Chemistry in Advanced Ceramics Processing*. Edited by R. J. Pugh and L. Bergstrom. Marcel Dekker, New York, 1994.
9. P.C. Hiemenz, *Principles of Colloid and Surface Chemistry*, 2nd ed.; p. 815. Marcel Dekker, New York, 1986.
10. R.J. Hunter, *Foundations of Colloid Science*, Vol. II; p. 1089. Oxford University Press, New York, 1989.
11. R.J. Hunter, *Introduction to Modern Colloid Science*; p. 338. Oxford University Press, New York, 1993.
12. M.N. Rahaman, *Ceramic Processing and Sintering*, 2nd ed.; p. 875. Marcel Dekker, New York, 2003.

13. E.M. Lifshitz, "The Theory of Molecular Attraction Forces between Solid Bodies," *Sov. Phys. JETP*, **2**, 73-83 (1956).
14. H.C. Hamaker, "The London-van der Waals Attraction between Spherical Particles," *Physica*, **4**, 1058-72 (1937).
15. F. London, "The General Theory of Molecular Forces," *Trans. Faraday Soc.*, **33**, 8-26 (1937).
16. L. Bergstrom, "Hamaker Constants of Inorganic Materials," *Adv. Colloid Interface Sci.*, **70**, 125-69 (1997).
17. R.H. French, "Origins and Applications of London Dispersion Forces and Hamaker Constants in Ceramics," *J. Am. Ceram. Soc.*, **83** [9] 2117-46 (2000).
18. R.H. French, R.M. Cannon, L.K. DeNoyer, and Y.M. Chiang, "Full Spectral Calculation of Non-Retarded Hamaker Constants for Ceramic Systems from Interband Transition Strengths," *Solid State Ionics*, **75**, 13-33 (1995).
19. J. Gregory, "Calculation of Hamaker Constants," *Adv. Colloid Interface Sci.*, **2** [4] 396-417 (1969).
20. D.B. Hough and L.R. White, "The Calculation of Hamaker Constants from Lifshitz Theory with Applications to Wetting Phenomena," *Adv. Colloid Interface Sci.*, **14** [1] 3-41 (1980).
21. J.N. Israelachvili, "The Calculation of van der Waals Dispersion Forces between Macroscopic Bodies," *Proc. R. Soc. London, A*, **331** [1584] 39-55 (1972).
22. J.N. Israelachvili, *Intermolecular and Surface Forces: With Applications to Colloidal and Biological Systems*; p. 296. Academic Press, San Diego, CA, 1985.
23. B.W. Ninham and V.A. Parsegian, "van der Waals Forces across Triple-Layer Films," *J. Chem. Phys.*, **52** [9] 4578-87 (1970).
24. B.W. Ninham and V.A. Parsegian, "van der Waals Forces: Special Characteristics in Lipid-Water Systems and a General Method of Calculation Based on the Lifshitz Theory," *Biophys. J.*, **10** [7] 646-63 (1970).
25. D.C. Prieve and W.B. Russel, "Simplified Predictions of Hamaker Constants from Lifshitz Theory," *J. Colloid Interface Sci.*, **125** [1] 1-13 (1988).
26. J.-L. Li, J. Chun, N.S. Wingreen, R. Car, I.A. Aksay, and D.A. Saville, "Use of Dielectric Functions in the Theory of Dispersion Forces," *Phys. Rev. B*, **71** [23] 235412 6pp. (2005).

27. C. Wohlfarth, *Static Dielectric Constants of Pure Liquids and Binary Liquid Mixtures*. Edited by M. D. Lechner. Springer-VDI-Verlag, Düsseldorf, Germany, 1991.
28. *CRC Handbook of Chemistry and Physics*, 70th ed. Edited by D.R. Lide CRC Press, New York, 1990.
29. R.H. Cole, "Dielectric Constants of Aliphatic Ketones," *J. Chem. Phys.*, **9** [3] 251-7 (1941).
30. R.J. Sengwa, K. Kaur, and R. Chaudhary, "Dielectric Properties of Low Molecular Weight Poly(ethylene glycols)," *Polym. Int.*, **49** [6] 599-608 (2000).
31. R.O. James, "Characterization of Colloids in Aqueous Systems," pp. 349-410 in *Advances in Ceramics*, Vol. 21, *Ceramic Powder Science*. Edited by G. L. Messing, J. W. McCauley, and K. S. Mazdiasni. American Ceramic Society, Westerville, OH, 1987.
32. G.A. Parks, "The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems," *Chemical Review*, **65** [2] 177-98 (1965).
33. P.D. Calvert, R.R. Lalanandham, M.V. Parish, J. Fox, H. Lee, R.I. Pober, E.S. Tormey, and H.K. Bowen, "Dispersion of Ceramic Particles in Organic Liquids," pp. 579-84 in *Better Ceramics through Chemistry II*. Edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich. Materials Research Society, Pittsburgh, PA, 1986.
34. B.I. Lee and J.P. Rives, "Dispersion of Alumina Powders in Nonaqueous Media," *Colloids Surf.*, **56**, 25-43 (1991).

VI. CONCLUSIONS

The applicability of DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory to non-aqueous suspensions has been demonstrated by the agreement of the predictions made from the calculated total potential curves with the viscosity measurements. DLVO theory is only applicable to suspensions in which the only significant dispersion mechanism is an electrostatic effect. For suspensions in which other mechanisms are present, the predictions set forth by DLVO theory are not valid. It is hypothesized that determination of the stabilization mechanism is possible by correlation of the viscosity of the suspension at a shear rate of 1.0s^{-1} to the shear thinning exponent of the suspension. It was found that if the suspension parameters described fell on the line, $y = 64.8[\exp(8.86x)]$, within a 95% confidence interval, the mechanism of dispersion for the suspension is electrostatic. Once the stability mechanism is determined to be solely electrostatic in nature, DLVO theory can be employed to predict stability via the total interaction potential between colloids. The total interaction potential was generated from the summation of the attractive and repulsive potentials as a function of separation distance between interacting particles.

The attractive potential was calculated using the Lifshitz method with the Ninham-Parsegian dielectric dispersion model. It was determined that the ultraviolet/visual characteristic relaxation frequency can be predicted using the bandgap, resulting in calculated Hamaker constants for oxide particles which are in agreement with the published values (using the Cauchy analysis). Using the bandgap to predict the attractive potential of non-oxide particles (e.g. diamond and SiC) results in significant error; however, since it was observed that the non-oxide colloids followed a similar linear trend, the error can be corrected. Other methods for predicting the value of the Hamaker constant have been proposed, the most commonly used being the Pugh approximation; however, using the proposed bandgap method has been shown to yield a more accurate value relative to the published values.

The relative magnitude of the Hamaker constant for a specific colloid in various mediums is sometimes approximated with the refractive index of the medium; the larger the refractive index of the medium, the smaller the Hamaker constant and subsequent van der Waals attractive potential. It has been theorized that a larger refractive index will effectively renormalize the boundary between particles resulting in a larger separation distance. This work demonstrates

that this approach is not valid as the Hamaker constant for most colloids does not vary in suspension medium according to the predicted trend. It is hypothesized that the respective prediction is problematic because the refractive index is only a measure of the electronic contribution to the dielectric dispersion and does not account for other relaxations in the microwave and infrared frequency ranges.

It is proposed that a more accurate prediction of the relative magnitude of the Hamaker constant can be made by determination of the ionic character of the bonding within the colloids. It was observed that the ionic character had an indirect relationship with ionic character of the bonds within the colloid for oxide particles. Colloids such as SiO_2 (ionic character of bonds = 1.54) had a relatively small Hamaker constant ($0.46 \times 10^{-20}\text{J}$), whereas rutile (ionic character of bonds = 1.9) had a larger Hamaker constant ($5.4 \times 10^{-20}\text{J}$). The basis of this observation is hypothesized to be due to the increased strength of the dipoles as the ionic character increases. This trend was not observed for the non-oxide or non-stoichiometric colloids.

It was observed through ζ -potential measurements that significant charge was developed on the surface of colloids in non-aqueous mediums. The development of surface charge in water is well understood through chemical reactions between the colloid surface and the hydronium and hydroxyl ions present. The development of charge in non-aqueous mediums; however, is not as well understood. It is hypothesized that, unlike in water where the dissociation (into hydronium and hydroxyl ions) first takes place and then surface reactions occur, in mediums in which the equilibrium constants of dissociation are much lower than that of water the medium molecules are first adsorbed onto the colloid surface in which dissociation occurs by proton exchange and then desorbs.

Commonly the stability of a suspension is correlated to the value of the ζ -potential. This resulted in a (now defunct) NIST standard which stated that a ζ -potential of 30mV was required for dispersion; however, this approach has been observed to be problematic. For example a large ζ -potential value was measured for the anatase/heptane suspension (112.5mV); however, the respective suspension was measured via viscosity to be unstable (agglomerated). The correlation between ζ -potential and suspension stability is inaccurate because it does not account for the degradation of the charge away from the colloid. The degradation of the charge is indirectly proportional to the thickness of the double-layer formed – the larger the double-layer, the less the charge degrades from the colloid into the bulk suspension. As polarity (dielectric constant) of the suspending medium increases, so does the thickness of the double-layer because of the ability of the medium to transmit the surface charge to distances further away from the colloid surface.

Therefore, a non-polar medium, such as heptane, may generate a large charge on the colloid surface; however, since the double-layer is relatively small, the repulsive potential generated from the surface charge will not become significant until interacting colloids are very close in proximity at which the van der Waals attraction between them is already significantly larger than the repulsive potential.

It was predicted from the total interaction potential that most suspensions would be unstable which was consistent with viscosity measurements. A thermal barrier was not observed for most unstable suspensions only a primary minimum resulted from the calculations. Suspensions in which a thermal barrier was associated had the possibility of being either stable, weakly flocculated, or unstable. If the energy introduced to the suspended colloids through Brownian motion was enough to overcome the thermal barrier, the interacting colloids would move into the primary minimum resulting in agglomeration; however, if the colloids could not overcome the thermal barrier they moved to the secondary minimum. The critical thermal barrier was measured to be approximately $2.0 \times 10^{-6} \text{ J/m}^2$ which was determined by viscosity measurements. If the colloids moved into the secondary minimum, one of two suspension types would result: 1) a weakly flocculated suspension characterized by a viscosity at a shear rate of 1.0 s^{-1} greater than the stable cut-off value (specific to each medium) and a shear thinning exponent greater than 1.0 or 2) a stable suspension characterized by a viscosity at a shear rate of 1.0 s^{-1} less than the specific viscosity cut-off value (1.1×10^4). It is hypothesized that the suspension type can be predicted by the equilibrium separation distance at the secondary minimum. If the separation distance is greater than approximately 40nm, a stable suspension will result; however, if the separation distance is less than approximately 40nm, a weakly flocculated suspension will result.

VII. APPENDIX A: ELLIPTICAL INTEGRAL PROGRAM

1.0 Program

Program used as a spreadsheet add-in (Excel, v.2010, Microsoft, Redmond, WA) is presented in Table A-I and Table A-III for the first (Equation A-1) and second (Equation A-2) order elliptical integrals respectively.

$$F(\phi, k) = \int_0^{\phi} \frac{d\theta}{\sqrt{1 - k^2 \sin^2(\theta)}} \quad \text{A-1}$$

$$E(\phi, k) = \int_0^{\phi} \sqrt{1 - k^2 \sin^2(\theta)} d\theta \quad \text{A-2}$$

These programs helped to produce an exact solution to the DLVO calculations.

Table A-I. Add-in Program Used to Calculate First Order Elliptical Integrals. k and ϕ are Expressed in Radians in the Worksheet.

Line	Program Step	Comments/Documentation
1	Function EllipInt1(ByVal phi As Double, ByVal k As Double) As Double	
2	Dim F As Double, phideg As Double	
3	phideg = 180 * phi / pi_	' convert phi to degrees
4	kdeg = 180 * k / pi_	' convert k to degrees
5	If phideg = 5 And kdeg = 6 Then F = 0.08726767	' Example of If Then statements to determine the value of the elliptical integral based on Table A-II. Repeats until the values entered for phi and k are found.
6	EllipInt1 = F	' Return the value
7	End Function	

Table A-II Example Table of Solutions to the First Order Elliptical Integral Adapted from Abramowitz¹

		ϕ		
		0°	5°	10°
k	0°	0.00000000	0.08726646	0.17453293
	2°	0.00000000	0.08726660	0.17453400
	4°	0.00000000	0.08726700	0.17453721
	6°	0.00000000	0.08726767	0.17454255
	8°	0.00000000	0.08726860	0.17454999

Table A-III. Add-in Program Used to Calculate Second Order Elliptical Integrals. k and ϕ are Expressed in Radians in the Worksheet.

Line	Program Step	Comments/Documentation
1	Function EllipInt2(ByVal phi As Double, ByVal k As Double) As Double	' 2 nd order elliptic integral – k in Rad, phi in Rad
2	Dim E As Double, phideg As Double	
3	phideg = 180 * phi / pi_	' convert phi to degrees
4	kdeg = 180 * k / pi_	' convert to degrees
5	If phideg = 5 And kdeg = 6 Then E = 0.08726525	' Example of If Then statements to determine the value of the elliptical integral based on Table A-IV. Repeats until the values entered for phi and k are found.
6	EllipInt2 = E	' Return the value
7	End Function	

Table A-IV. Example Table of Solutions to the Second Order Elliptical Integral Adapted from Abramowitz¹

		ϕ		
		0°	5°	10°
k	0°	0.00000000	0.08726646	0.17453293
	2°	0.00000000	0.08726633	0.17453185
	4°	0.00000000	0.08726592	0.17452864
	6°	0.00000000	0.08726525	0.17452330
	8°	0.00000000	0.08726432	0.17451587

2.0 References

1. United States National Bureau of Standards, Applied Mathematics Series, Vol. 55, *Handbook of Mathematical Functions: With Formulas, Graphs, and Mathematical Tables*; p. 1046. Edited by M. Abramowitz and I.A. Stegun. United States Government Print Office, Washington D.C., 1964.