CALCULATION OF HAMAKER CONSTANTS IN NONAQUEOUS FLUID MEDIA

Nelson Bell and Duane Dimos
Ceramic Materials Department, Sandia National Laboratories, 1515 Eubank Blvd. SE, MS 1411,
Albuquerque, NM 87123

ABSTRACT

Calculations of the Hamaker constants representing the van der Waals interactions between conductor, resistor and dielectric materials are performed using Lifshitz theory. The calculation of the parameters for the Ninham-Parsegian relationship for several non-aqueous liquids has been derived based on literature dielectric data. Discussion of the role of van der Waals forces in the dispersion of particles is given for understanding paste formulation. Experimental measurements of viscosity are presented to show the role of dispersant truncation of attractive van der Waals forces.

INTRODUCTION

Thick film pastes are complicated examples of colloidal processing and engineering. The desired rheological characteristics for thick film printing include a shear thinning viscosity to allow flow during printing and a yield stress to maintain printed feature definition. These properties are achieved through control of the range and magnitude of interparticle forces. All similar materials experience attractive forces due to permanent or induced dipolar interactions, and the effect of these interactions between materials is expressed macroscopically in terms of the Hamaker constant, A_{132}. This attractive force generates an agglomerated particle network that resists flow. In order to make a suspension fluid, a stabilizing mechanism must be employed that controls the magnitude of the attractive forces between the particles to give the desired rheological behavior. By keeping particles at a fixed separation distance, the strength of their attraction can be controlled. The Hamaker constant provides a baseline for understanding how much separation is required. Understanding the strength of the Hamaker constant helps determine the type and properties of the stabilizing mechanism needed to form an effective thick film paste composition.

The Hamaker constant was first calculated by summing the interactions between the dipole-pairs in a material [1]. This laborious procedure was greatly simplified when Lifshitz described how the dielectric response function of a material could be used to perform the same function more accurately as it incorporates many-body effects directly into the calculation [2]. Assuming materials to be continuous media, the Ninham-Parsegian (N-P) imaginary function can be used to represent the dielectric response as a function of frequency [3-5]. This N-P representation has no direct physical basis but can be constructed based on knowledge of the static dielectric constant, index of refraction, and infrared, ultraviolet and microwave absorption spectra. One of the properties of the N-P relationship is that it is evaluated at discrete imaginary frequencies which are distributed so that the ultraviolet and (to a lesser degree) infrared spectra dominate the determination of the Hamaker constant. Accuracy of the calculation therefore depends greatly on the accuracy of the IR and UV spectra used to construct the N-P function for the material.

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Most calculations of Hamaker constants have focused on aqueous media. Much of the reason for attention being paid to water is its environmentally benign nature. Yet, the majority of thick film pastes used in the electronics industry are in nonaqueous solvents, and the availability of information for these systems are not common in the literature. It is the drive of this work to fill the gap in the literature of the functions required to calculate Hamaker constants in nonaqueous media. In doing so, the role of dispersants in these media to control rheological response will be improved, and the possibility of tailoring solid and liquid to provide esired rheological properties can be explored.

EXPERIMENTAL

Rheological measurements were performed with a Bohlin CS-10 rheometer[1]. Silver slurries[2] were prepared at 40 volume % in methanol and isopropanol. Pluronic F68[3] dispersant was added at 0.4 weight % to powder to evaluate the control of interparticle force on rheological response. This dispersant is a triblock copolymer of polyethylene oxide stabilizing blocks bonded to an adsorbing block of polypropylene oxide. Experiments were performed using a 60 second preshear at 400 rpm followed by a hold time of 30 seconds. Tests were run from low shear rate to high and back to zero.

The parameters for the Ninham-Parsegian expression for liquids can be found in a variety of literature sources. Water has been most extensively characterized, and the spectral parameters for water are given in [5]. Six infra-red and five ultraviolet damped oscillators with a single Debye microwave relaxation represent the dielectric behavior very well. However, this level of detail is hard to compile for most nonaqueous solvents. The static dielectric constant and index of refraction at the sodium D line are commonly tabulated [6], and the infra-red adsorption spectra for many liquids are relatively easy to find [7]. The microwave parameters for several liquids are referenced in the compilation of Buckley and Maryott [8]. Determination of the ultraviolet characteristics for several solvents has proven to be more difficult. This is a serious complication as the ultraviolet terms are the most critical for calculating the Hamaker constant. In the absence of a full spectra, UV relaxation is commonly represented by a single oscillator of magnitude equal to $n^2 - 1$. The UV adsorption edge was chosen as the critical frequency of this oscillator and damping terms were omitted [6]. Further searches are being performed to determine the UV spectra for these nonaqueous fluids and refine the parameters for Hamaker constant calculation.

From the collected data, the oscillator strengths were determined by the changes in the value of the real dielectric constant between spectral regions. The microwave strength can be determined directly from [8]. Groups of peaks located very closely together in the infra-red spectrum are represented by a single oscillator and damping terms were omitted. The index of refraction was used to determine the magnitude of the transition between the microwave and visible region due to adsorption in the IR, and individual oscillator strengths were assigned based on the area of each IR adsorption. The ultraviolet adsorption was represented by a single oscillator at the UV adsorption edge. This collected data is presented in Table 1.

The optical parameters for solids have been tabulated in several sources that can be used to fit the oscillator models for dielectric behavior [5,9,10]. Most metal oxides can be fit in a

Table 1. Spectral Parameters for the Ninham-Parsegian expression of $\varepsilon(i\xi)$ for Nonaqueous Solvents.

Name	Type	Dielectric Constant	C_{MW}	ω_{MW} (rad/sec)	$C_{IR}(\#)$	$\omega_{IR}(\#)$ (rad/sec)	n	C_{UV}	ω_{UV} (rad/sec)
Methanol	Amphiprotic	33.64	27.64	2×10^{12}	0.254 0.123 1.042 2.801	3.0579×10^{13} 4.149×10^{13} 8.682×10^{13} 1.007×10^{14}	1.3288	0.76571	9.1885×10^{15}
1-Propanol	Amphiprotic	20.8	17.4	3×10^{9}	0.2134 0.1778 0.3808 0.70977	3.148×10^{13} 4.317×10^{13} 8.8019×10^{13} 9.977×10^{13}	1.3850	0.91823	8.9698×10^{15}
2-Propanol	Amphiprotic	20.18	17.12	1×10^{10}	0.0198 0.05927 0.1441 0.1801 0.2208 0.53462	2.4343×10^{13} 2.842×10^{13} 3.4656×10^{13} 4.125×10^{13} 8.8739×10^{13} 9.9172×10^{13}	1.3776	0.89778	9.1885×10^{15}
1-Butanol	Amphiprotic	17.84	14.84	2×10^{9}	0.13545 0.13233 0.26674 0.50743	3.1778×10^{13} 4.2871×10^{13} 8.7840×10^{13} 9.9172×10^{13}	1.3993	0.95804	8.7612×10^{15}
2-Butanol	Amphiprotic	17.26	13.32	2×10^{9}	0.2582 0.2185 0.4767 0.9931	2.9979×10^{13} 4.1132×10^{13} 8.9039×10^{13} 1.0037×10^{14}	1.3978	0.95385	7.2448×10^{15}
Benzene	Inert	2.28	N/A	N/A	0.00969 0.00561 0.0114	2.0146×10^{13} 4.437×10^{13} 9.144×10^{13}	1.5011	1.25330	6.7757×10^{15}
Toluene	Inert	2.38	N/A	N/A	0.0642 0.02295 0.0545	2.1825×10^{13} 4.4849×10^{13} 9.0778×10^{13}	1.4961	1.23832	6.6326×10^{15}

similar manner to the liquids. Values for alumina and barium titanate were taken from the compilation of Bergstrom [5]. Parameters for silver were taken from Parsegian and Weiss [11]. The parameters have been converted from eV to rad/sec. The first term has no critical frequency, and it represents the hyperbolic dependence of the conduction electrons.

Table 2. Spectral Parameters for the Ninham-Parsegian expression of $\varepsilon(i\xi)$ for Solid Materials.

Name	Dielectric Constant	Index of Refraction	C_j	ω_j (rad/sec)	g_j (rad/sec)	Source
Silver	∞	--	2.1209×10^{32}	--	--	16
			1.51997	7.8997×10^{15}	2.8864×10^{15}	
			0.54527	2.3547×10^{15}	8.20349×10^{15}	
			0.17327	3.4333×10^{16}	5.46899×10^{15}	
			2.24565	5.2563×10^{16}	1.43105×10^{17}	
Alumina	10.1	1.753	2.072	2.0×10^{16}	--	5
			7.03	1×10^{14}	--	
Barium Titanate	o 3600	2.284	4.218	0.841×10^{16}	--	5
			3595	$0.7\text{-}1.0 \times 10^{14}$	--	

RESULTS

Using the parameters from Tables 1 and 2, the Hamaker constant between identical particles in various liquid media was determined by the N-P method [3-5]. These values are given in Table 3.

Table 3. Hamaker Constants between Identical Particles in Various Solvents

Solvent	Silver (zJ)	Alumina (zJ)	Barium Titanate (zJ)
Water	149.1	36.9	106.8
Methanol	175.2	84.4	142.8
1-Propanol	168	76.0	134.4
2-Propanol	224.5	149	203.9
1-Butanol	167.3	75.0	133.2
2- Butanol	175.4	84.7	142.5
Benzene	166.4	77.0	131.5
Toluene	168	78.6	133.3

From the values in Table 3, there is a general trend regardless of solvent that ranks the Hamaker constants in the order silver > barium titanate > alumina. This trend relates to the material dielectric constant which results from Keesom and Debye electrostatic interactions. The London (dispersive) interactions that affect the IR and UV adsorption cannot compensate for the difference in static properties. The high magnitudes of the dielectric constant for barium titanate (3600) and of silver (infinity) makes it unlikely that any solvent exists which will match the dielectric properties of these materials and cause a minimum in the Hamaker constant. Alumina however has a low dielectric constant, so the possiblity to choose a solvent that minimizes van der Waals interactions is available.

In comparison of the solvents, the values for each solid material with water as the solvent can be expected to be more accurate than the nonaqueous solvents due to the higher degree of characterization of the dielectric spectra available for water. No solvent that was evaluated has a Hamaker constant lower than water, and in general they are significantly higher. Most of the

nonaqueous values are of comparable magnitude with the exception of 2-propanol. The high value of A_{132} for 2-propanol predicts that with a similar dispersing mechanism, values of shear stress and viscosity will be higher in 2-propanol versus another solvent.

To test this hypothesis and the accuracy of the parameters used in calculation, silver dispersions were made in methanol and 2-propanol using a nonionic dispersant recommended for use in water and alcohols. The viscosity data was normalized for the intrinsic solvent viscosity, and the samples are compared in Figure 1. Contrary to the Hamaker constant prediction, the attractive forces in methanol seem higher than in 2-propanol. Reasons for the discrepancy include: the Hamaker values for 2-propanol are too high, there may be electrostatic forces present in the 2-propanol, or the dispersant may have different solvation characteristics in each solvent. The viscosity curves have the same qualitative behavior and exhibit little hysteresis between the rising and falling shear rate test. This suggests that the dispersant is behaving similarly between the two solvents, but it does not rule out the possibility that there may be differing adsorbed amount of polymer or a difference in the extension of the polymer from the surface. However, the estimations used in the ultraviolet spectra of 2-propanol may need to be corrected to give the most correct values. Further examination of the surface chemistry of the silver powder in each solvent and the behavior of the dispersant need to be performed before definite answers can be concluded.
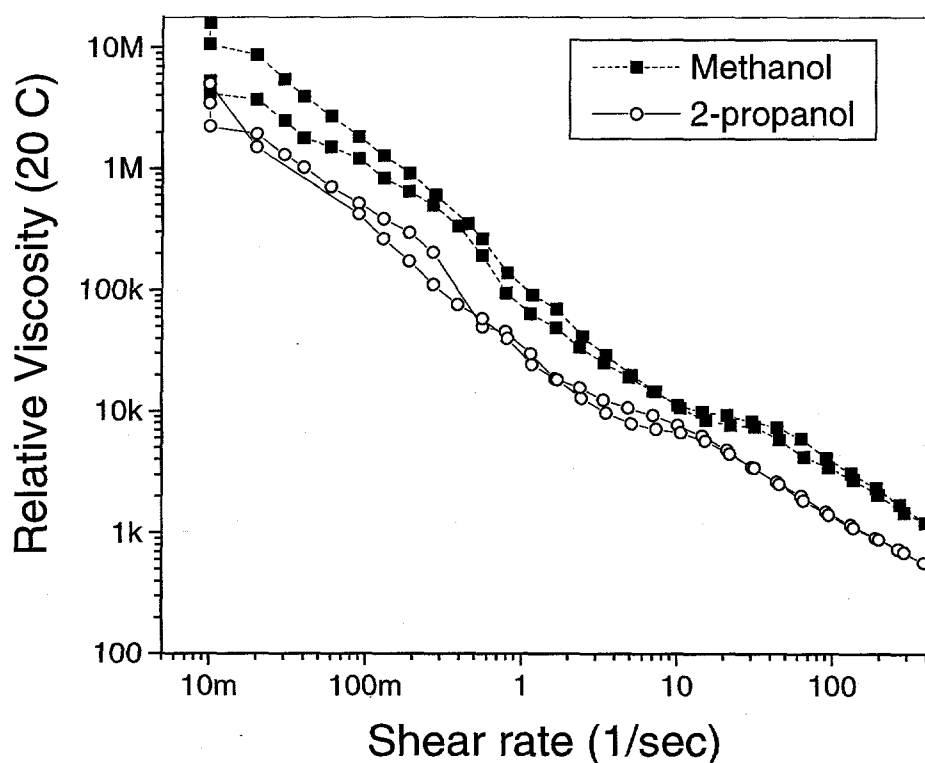

Figure 1. Relative viscosity comparison of silver powder dispersed with Pluronic F68 in methanol and isopropanol.

CONCLUSIONS

Terms needed for calculating the Hamaker constant of several nonaqueous liquids have been collected from the literature, and the Hamaker constant for three materials systems have been calculated for identical particles in these solvents and in water. Within each solid system, the Hamaker constant scales with dielectric constant. The nonaqueous solvents were calculated to have larger Hamaker constants than water, but their accuracy could be improved by using more accurate representations of the ultraviolet adsorption spectra. The examination of two nonaqueous solvents for differences in van der Waals attractive forces did not agree with values of the Hamaker constant. Reasons for the discrepancy require more investigation of each system.

ACKNOWLEDGEMENTS

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