Upconverting Nanoparticle Security Inks Based on Hansen Solubility Parameters

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Abstract

Hansen solubility parameters (HSPs) provide quantitative insight into the surface chemistry of nanomaterials, enabling a unique approach to ink formulation. In this work, HSPs of upconverting $NaYF_4$ nanoparticles were subjected to a broad spectrum solvent testing method, and a binary solvent gradient (BSG) method to elucidate their HSPs. The outcome of these experiments enables the selection of a number of potential solvents to meet printer and substrate requirements.

Introduction

Ink formulation aims to ideally disperse a functional material by selection of solvents and dispersants that can achieve a minimization of mixing free energy, meet printer viscosity and surface tension requirements and promote ideal substrate interactions[1]. Organic functional materials (dyes, proteins and polymers) have relatively wide ranges of interaction with many solvents because of their conformational capabilities, resonances, uniquely small dimensions, etc. Inorganic nanomaterials lack the variable nature of organics because of their confined structures, limiting traditional solvents that will disperse them. During nanoparticle synthesis capping agents are used to control size, morphology and coalescence of nanoparticles. These surface adhered molecules can alter the nanoparticle interaction with surrounding solvents to be closer to that of an organic material, enabling interactions with a relatively larger number of solvents. Further surface modifications, surfactant stabilization and other solution stabilizers can be added during an ink formulation to then optimize intermolecular interactions between the nanomaterial and solvents[2].

HSPs describe intermolecular interactions as a combination of dispersive (δd), polar (δp) and hydrogen bonding (δh) forces[3]. Materials larger than the molecular scale are described by a fourth interaction parameter, R_0, to describe the variance in δd, δp and δh for a given material. Polymers, dyes and other organic materials have large R_0 values relative to inorganics because of conformational variances, radii of gyration, etc. Inorganic nanomaterials show few of these variations due to the nature of their static geometries, leading to typically small R_0 values[4]. If the HSPs of a material are known, it is possible to identify solvents that will disperse the material by calculating the following:

$$R_a{}^2 = 4(\delta d_2 - \delta d_1)^2 + (\delta p_2 - \delta p_1)^2 + (\delta h_2 - \delta h_1)^2 \quad (1)$$

$$RED = \frac{R_a}{R_0} \quad (2)$$

A three dimensional solubility space can be constructed with axis of δd, δp and δh. Solvent molecules are plotted as individual points, while solutes are typically plotted as spheres with radius R_0. R_a defines the distance between two points in solubility space, and RED determines if a point lies within the interaction sphere of the solute. If RED is less than one, the solvent will disperse the solute, and if RED is greater than one the solvent will not disperse the material. Combinations of solvents can yield new HSPs based on a volumetrically weighted average.

$$\delta X_{mix} = \sum_{i=1}^{n} \delta X_i \cdot V_i \quad (3)$$

Where δX is one of the interaction parameters (δd, δp or δh), and V is the volumetric fraction of the i^{th} solvent in the mixture.

When the HSPs of nanoparticles are characterized, a number of solvents are revealed to have RED less than one, resulting in dispersion of the species. Once a nanoparticle's HSPs have been characterized, solvents or solvent mixtures can be chosen with RED less than one, while meeting a printing system's rheological and surface chemistry requirements. Here, we characterize the HSPs of oleic acid capped $NaYF_4$ nanoparticles as a case study for this approach to ink formulation.

Experimental

Nanocrystal Synthesis

Beta-phase $NaYF_4$ nanoparticles were synthesized by Baride using a previously described method[5,6] with slight modification. Oxides of yttrium, ytterbium, and erbium were refluxed with a mixture of water and acetic acid to convert the oxides into acetates. The lanthanide acetate solution was heated under vacuum in the presence of oleic acid for 30 minutes at which point the metal acetates converted to oleates. In a flask, a mixture of oleic acid, 1-octadecene, sodium acetate and NaF was heated under vacuum to remove acetic acid formed by the conversion of sodium acetate to sodium oleate. The reaction vacuum was replaced with Ar gas and the reaction temperature raised to 320°C. The lanthanide oleate precursor solution was then injected into the reaction mixture and heated further at 320°C to produce upconverting particles. Product identity and phase purity was confirmed by powder XRD and TEM analysis. The resulting oleate-capped particles are hexagonal right prisms, approximately 70.8 ± 11.5 nm across the hexagonal face (edge-to-edge) and 66.5 ± 6.8 nm along the *c* axis.

Broad Spectrum Solvent Testing

3 mg of dried particles were added to 3 mL vials followed by the addition of 2 mL of each test solvent to obtain a rough estimate of nanoparticle dispersion. Test solvents included toluene, chloroform, methyl benzoate, mesitylene, dodecane, acetone, methanol, ethanol, n-propyl acetate, ethyl propionate, ethylene glycol monobutyl ether, and methyl cyclohexane. These vials were sonicated for one minute and then left undisturbed for three days. At this time, each vial was exposed to 980 nm light to determine dispersion of nanoparticles, where dispersion was defined as uniform luminescence throughout the vial, and settling was defined

as weak luminescence in the bulk solvent with strong luminescence at the bottom of the vial, as illustrated in Figure 1.

Binary Solvent Gradient Testing

Experimental protocol for the BSG method are the same as the broad spectrum method, with the exception that the solvents are a mixture of one good solvent and one bad solvent as per Machui's method[7], varying the good:bad ratio by 10 vol% per vial (ex. 90:10, 80:20, 70:30 mixtures). The purpose of this approach is to form three lines of discreet points in solubility space that are closely spaced to more accurately identify the interaction radius of the solute. Solvent mixtures tested were: acetone and toluene, methyl benzoate and toluene, and methyl benzoate and dodecane.

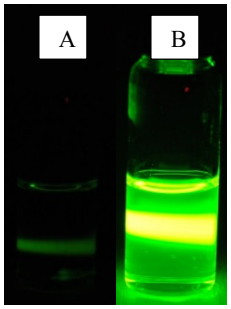

Figure 1. *Example of poor solvent dispersion (A) and good solvent dispersion (B) during dispersion testing.*

Results

Dispersion results were plotted using Hansen Solubility Parameters in Practice (HSPiP) software[7] to identify HSPs of various solvents, and interaction spheres of the upconverting particles for both broad spectrum and BSG methods. Broad spectrum solvent testing results are shown in Figure 2, where particles remained dispersed in toluene, dodecane, mesitlyene, ethyl propionate, methyl cyclohexane, and chloroform. These results yielded HSPs for oleic acid capped $NaYF_4$ as δd:16.6 δp:3.3 δh:2.5 R_0:4.4

Binary solvent gradient testing results are plotted in Figure 3. Particles settled out of the toluene/acetone mixture when acetone was greater than 30 vol%, when methyl benzoate was greater than 50 vol% in the methyl benzoate/toluene mixture, and when methyl benzoate was greater than 30% in the methyl benzoate/dodecane mixture. The BSG results reduced the HSPs to δd:18.47 δp:5.97 δh:2.85 R_0:2.8.

Discussion

The results of the broad spectrum test show slightly lower dispersive, polar, and hydrogen bonding values while having a significantly larger interaction radius than those of the binary solvent gradient method because of the reduced point-to-point resolution for the broad spectrum method. From an ink formulation perspective, the BSG method rules out a number of solvents that may perform ideally for a short period of time, as predicted by the broad spectrum method.

The values obtained from the BSG method identify a number of potential solvents that will disperse the particles. Similarly, the same set of solvents can also be used to solubilize a polymer, or another nanomaterial, while meeting the rheological requirements of the printer. These combinations of polymer and particles are typically easy to obtain due to the large R_0 of most polymers. For comparison, a typical polymer will have an interaction radius anywhere from 4 to 20,[8] while the interaction radius for these nanoparticles is much smaller. Furthermore, if none of the potential solvents can achieve these values, solvents outside the sphere can be mixed with very good solvents to still produce a dispersive mixture based on Equation 3.

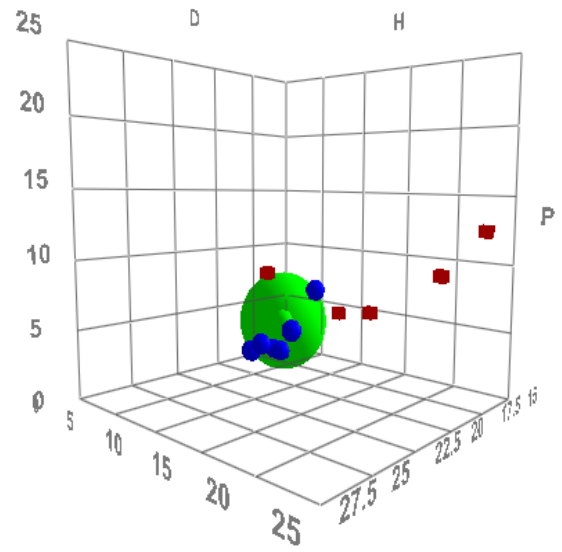

Figure 2. *Broad spectrum results plotted in solubility space. Blue spheres indicate good solvents, red cubes indicate poor solvents and the green sphere indicates the nanoparticle interaction volume*

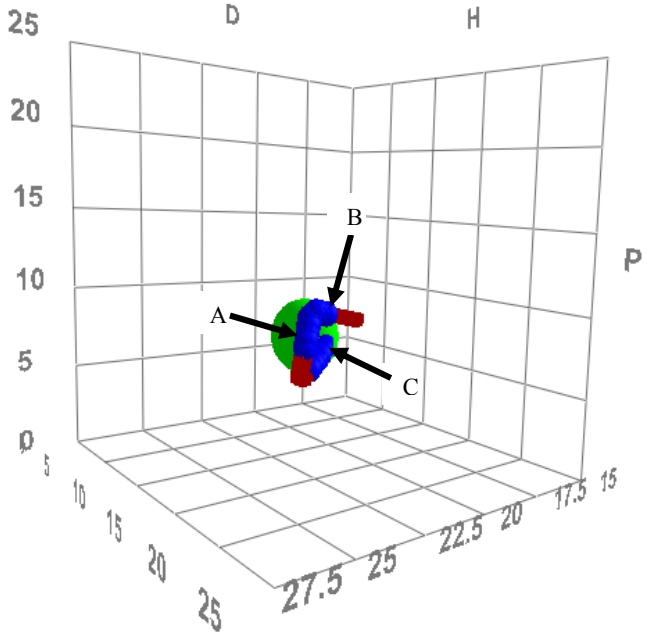

Figure 3. *BSG results plotted in solubility space. A is the methyl benzoate/toluene mixture, B is the acetone/toluene mixture, and C is the methyl benzoate/dodecane mixture*

Conclusion

Broad spectrum and BSG methods of HSPs characterization were employed to identify the HSPs of oleic acid capped $NaYF_4$ nanoparticles. Values obtained show that the particles are dispersed by mildly polar molecules that exert some hydrogen bonding forces,

with a fairly selective interaction radius. These values point to solvents such as a mixture of 90 vol% toluene and 10 vol% methyl benzoate for an aerosol jet system, while most solvent combination for a piezo inkjet system would not disperse these particles (ex. water or ethylene glycol). The general approach for HSPs characterization for ink formulation shows that, with a selective number of experiments, the process can be moved away from trial and error approaches.

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Author Biography

Jacob Petersen received his BS in Materials Science and Engineering from the University of California Merced (2012), his MS in Materials Engineering and Science from the South Dakota School of Mines and Technology (2014), and is currently pursuing his PhD in Materials Engineering and Science at the South Dakota School of Mines and Technology). His research focuses on synthesis of novel nanomaterials for various applications in security printing and printed composites.