TERNARY PHASE DIAGRAM OF
OCTANE-1-OCTANOL-1-OCTYLAMINE

By

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A thesis submitted to the
Graduate School-New Brunswick
Rutgers, The State University of New Jersey
In partial fulfillment of the requirements
For the degree of
Master of Science
Graduate Program in Food Science
Written under the direction of
Dr. Michael A. Rogers
And approved by

New Brunswick, New Jersey
May 2015
ABSTRACT OF THE THESIS

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Structuring liquid oils with molecular gels as a novel strategy, to replace saturated and trans fat, has become an intense field of study. Molecular gels are thermally reversible, semi-solid materials, which can self-assemble into three dimensional (3D) fibrillar networks. These self-assembled fibrillar networks (SAFiNs) formed via non-covalent interactions by low molecular weight organogelators (LMOGs) are postulated as alternative structurants for liquid oils. However, till now there is no such applications in the food industry due to a series of issues, including a lack of understanding on the mechanism of gelation. Numerous trials and experiments have been done to elucidate the mechanism of gelation process. Hansen solubility parameters (HSPs) are found to correlate with gelation behavior of 12-hydroxystearic acid (12HSA), which can gel a wide range of organic solvents. However, most research has focused on a single solvent-gelator system. In this study, the effect of ternary solvent mixtures using, octane, 1-octanol and 1-octylamine, were investigated at different ratios with 12HSA as the gelator to elucidate effects on structure, thermal and rheological properties.
This thesis is dedicated to:

My parents

Jingyao Liu & Yan Liu
ACKNOWLEDGMENTS

First and foremost, I would like to express my deepest appreciation to my advisor Dr. Rogers for his patience and support on my research. Without his guidance and encouragements, it is impossible for me to complete my master degree in food science. He is my mentor, my advisor, and my friend. For the past two year in my graduate study, he dedicated his love and life to inspire and guide us. Most importantly, his enormous passion for science always fills me with strength and hope. When I first started in the lab, I had many difficulties in my experiment. The study of molecular gels was new to me. It required a large amount of reading to understand the theory and mechanism behind the experiments. I always felt stressed and lost when I could not figure out the solutions. Dr. Rogers was the one who not only explained the confusing articles for me, but also taught me methods to solve my problems. Without his inspiration, there would have been no way for me to write a scientific paper and finish my thesis. Besides his generous support on my study, Dr. Rogers also brightens my life with his great personality. Always being positive in life and being a doer instead of a dreamer is what he showed us as a role model.

Beside my advisor, I would to like to thank Dr. Yam who has been always encouraging me and guiding me through difficulties. There was time I felt lost and did not do well in my study. As the graduate student director, Dr. Yam was the one who taught me how to bounce back when I hit the bottom of my life. I would also like to express my gratitude to Dr. Corradini, who taught me mathematica and made a great contribution to my paper. I would also like to extend my thanks to all the faculty members. They have all played important roles in the past two years of my graduate school life.

I send my heartfelt appreciation to Vi Dao, whose support and encouragement gave
me strength to overcome the obstacles that came my way.

Last but not least, I would like to express my sincere gratitude to my beloved parents. I could not imagine what would I be without their support and understanding. It was not easy for them to let their only son leave far from home to live in the US. They gave me this opportunity to observe the world and chase my own dreams. There is no word can express my love for them.

In the end, I would like to thank my friends who have always been there for me when I need help. Your company made my life happy and wonderful! Thank you all!
PREFACE

The research presented in this thesis was conducted in the Department of Food Science, School of Environmental and Biological Sciences, Rutgers, The State University of New Jersey. It is a result of my work during the period between September 2012 and May 2014.

Chapter four of is co-authored by Dr. Michael A. Rogers. With pride, this chapter has been published in The Journal of Colloid and Polymer Science: entitled “Self-Assembly of 12-Hydroxystearic Acid Molecular Gels in Mixed Solvent Systems Rationalized using Hansen Solubility Parameters”, (DOI:10.1007/s00396-014-3480-9), Published: Dec 11, 2014.
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1.0 INTRODUCTION

Coronary heart disease, associated with consuming high amounts of both saturated and trans fats remains a major health concern for society. [1] These fats are recognized as ‘bad’ fats and have been very well studied over the past 50 years. [2] There is a large data set of quantitative data identifying the relationship between the intake of the ‘bad’ fats and cardiovascular disease. [3] It has been reported that an increased intake of saturated and trans fats can cause increased levels of low-density lipoprotein (LDL) and decreased levels of high-density lipoprotein (HDL). [1, 4] Having optimal levels of both lipoproteins is crucial to health. If there is too much LDL in the blood, plague builds up inside the coronary artery walls and may impede blood flow. It can cause an increased risk of cardiovascular disease when plague dislodges. [5, 6]

For almost 100 years, hydrogenation was a popular way of transforming liquid oil to solid fat, which has more desirable physical properties, such as texture and mouth feel. [1, 2] After hydrogenation, liquid vegetable oils turn into solid or semi-solid fat with a high melting point. Hydrogenation reduces cost as hydrogenated vegetable oils are cheaper than animal source fats and it increases the shelf-life, as saturated solid fat are more oxidatively stable compared to unsaturated oils. [7] However, hydrogenation not only increases the saturation of carbon-carbon double bonds but may also convert cis geometric isomers to trans isomers. [2] It has been reported that approximately 3% of total calorie consumption in the US is from the industrially produced trans fatty acids. [8] This exceeds the limit proposed by the Dietary Guidelines Advisory Committee, which states that trans fat consumption should be no more than 1% of total calorie consumed. [3]
The Food and Drug Administration (FDA) required the mandatory labeling of “trans fat” on Jan 1, 2006. [9] Since then, food manufactures started trying to reduce the levels of saturated trans fat in order to meet the authorities and customers expectations. Thus, replacing the ‘bad’ fats, including saturated and trans fats, with unsaturated good fats has become a very active field of study in the past few years. [2, 10, 11] However, it is difficult to eliminate the saturated and trans fats without sacrificing the quality of the food products, mainly because the saturated and trans fats serve to structure the liquid components and maintain the rigidity of food products. [10] A novel strategy to reduce and/or eliminate saturated and trans fats from our diets is to find an alternative oil structuring strategies. A few compounds including waxes, ceramides, organogels and monoacylglycerides etc. were found to be good alternative structurants. Among them the small-molecule organogelators have drawn the greatest attention with regards to their ability to form self-assemble crystalline structures that can trap oil. [11-16]

Organogels, as one type of soft matter, are thermoreversible semi-solid materials which can maintain as much as 95% of organic liquids through its three-dimensional (3-D) self-assembled fibrillar networks (SAFiNs). [13, 14, 17-19] A wide range of applications have been developed in the past few decades due to their capability to immobilize organic liquids, such as recovery of oil spills, [10] controlled drug release, [20] light harvesting. [21] Not surprisingly, food scientists and technologists have studied this technology as an alternative oil structuring method as well. [10, 11]
It has been reported that LMOGs self-assemble through physical, non-covalent internal interactions including: hydrogen-bonding, [22-24] pi-pi stacking, [25] dipole-dipole interactions, [26, 27] and London dispersion forces. [28] LMOGs self-assemble into SAFiNs, which structures the edible oils into solids. [11, 29] Thus, it allows us to incorporate the 3D network of SAFiNs to alter the physical properties of edible oils achieving similar textures as hard stock crystalline triacylglycerols (TAG). [2, 29] The major limitation to these gels lies in the uncertainty of the physics of the gelation process, as well as the lack of suitable gelators that are food grade, effective and generally recognized as safe (GRAS). [11] To further discover the potential of the SAFiNs, as novel alternative edible oil structurant, an intimate, thorough understanding of gelation behavior is needed.

Given the fact that organogels form only when there is a balance between gelator-gelator and gelator-solvent interactions, solvent parameters, such as Hansen solubility parameters (HSPs), etc., have been well correlated to gelation behavior. [13-16] Studies over the past few years, with regards to HSPs and organogels, have been met with mixed success. HSPs, which consist of dispersive interactions ($\delta_d$), polar interactions ($\delta_p$), and hydrogen-bonding interactions ($\delta_h$), are the most promising tools for predicting 12HSA gelation behavior. [14] Most strong correlations are found between $\delta_h$ and gelation ability. For instance, too high of a hydrogen-bonding interactions between a gelator and a solvent can interfere with gelation process resulting in solution, as the gelator becomes too soluble in the solvent. [16, 19] However, the quantification of the hydrogen-bonding interactions is solely dependent on the $\delta_h$ of one single solvent, as the majority of the research has focused on a gelator mixed in a single solvent. To date, only a handful of studies have been
completed on a mixed dual solvent systems using HSPs. [30, 31] In this study, the
effect of ternary solvent mixtures using octane, 1-octanol and 1-octylamine—were
employed at different ratios to investigate the effects on structure, thermal and
rheological properties of a 12HSA/solvent blend.
2.0 OBJECTIVES

In order to understand the solvents effects on organogel formation, the objective of this study is: To examine the effect of ternary solvent mixtures at different ratios on structure, thermal and rheological properties of 12HSA/solvent blends.
3.0 LITERATURE REVIEW

3.1 Gels

3.1.1 Definition

Gels are a commonly used term in our daily life. They have a huge range of applications that can be found in personal care products including bath gels, rejuvenating gels, hair gels, etc. [32, 33] They are also common occurrence in foods such as egg whites, gelatin, pectin. When focused on organogels, which is one type of gel, the potential of its applications have been reported in the field of pharmaceuticals, cosmetics, and food. [2, 10, 11, 34, 35] With no doubt, gels are everywhere. However, the definition of gel is so simple. The question “what is gel?” has been brought up since 1861 by Thomas Graham, who is known as “Master of the Mint”. He viewed gels as a colloid medium for liquid diffusion, which possesses energy to maintain its structure. [36]

65 years later, D. Jordan-Lloyd published the article ‘The problem of gel structure’ where she wrote

“the colloidal condition, the gel, is one which is easier to recognize than to define, and even recognition is confused by the fact that the limits between gel and sol, on the one hand, and gel and what may be termed curd, on the other, are not precise, but consist of a gradual change”. [37]

Gels were classified into two categories based on her review on the structure of gels -- heat-reversible gels and heat-irreversible gels. [38] She also pointed out that a gel must have two components, one is liquid and the other is solid. [17] Her definition
provided a basic understanding of gels even though there was one thing she did not make clear and that was not all colloids are gels and not all gels are colloids. Another common definition of a gel that she defined was: “if it looks like Jello, it’s a gel”. [37] In 1949, Hermans carried on the progress of definition to the point where he clarified that gels: “…are coherent colloid disperse systems of at least two components exhibit mechanical properties characteristic of the solid state…” and “…both the dispersed component and dispersion medium extend themselves continuously throughout the whole system”. [39] Compared with Hermans’s detailed definition, in 1961, Ferry proposed a less complicated version: “a gel is a substantially diluted system which exhibits no steady state flow”. [40] Based on these definitions, Weiss and Terech finalized two features that can be used to classify a gel: “(1) it has a continuous microscopic structure with macroscopic dimensions that is permanent on the time scale of an analytical experiment and (2) it is solid-like in its rheological behavior, despite being mostly liquid”. [17] So far great contributions have been made by a number of scientists to define a gel. However, it is difficult to draw a final conclusion from the scientists with different backgrounds, in addition, every rule seems to have exceptions. Therefore, the scientific definition should be updated from time to time, when exceptions are found. [38]

3.1.2 Classification

The classifications of gels vary, as the thermal, rheological and structural properties of gels are different. [38] In the early 90s, German chemist Wolfgang Ostwald, proposed gel classifications according to the matrix phase, solvent phase and crosslinkage type shown in Table 3-1 (A-C).
### A  Basis  Type  Examples

<table>
<thead>
<tr>
<th>Solvent phase</th>
<th>Solid-liquid</th>
<th>Hydrogel (water solvent)  Organogel (organic solvent)  Liogel (oily solvent)  Alcogel (alcohol solvent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid-gas</td>
<td></td>
<td>Xerogel (air)  Aerogel (air)</td>
</tr>
<tr>
<td>Solid-solid</td>
<td></td>
<td>Polymer-gel (polymer)</td>
</tr>
</tbody>
</table>

### B  Basis  Type  Examples

<table>
<thead>
<tr>
<th>Crosslinkag</th>
<th>Covalent</th>
<th>Chemical gelation:  Covalent crosslinking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-covalent</td>
<td>Physical Gelation:  -Coulombic interaction  -Hydrogen bonding  -Coordinate bonding  -Hydrophobic bonding</td>
</tr>
</tbody>
</table>

### C  Basis  Type  Examples

| Constituent phase | Surfactant bilayers | o/w Creams  w/o Creams  Amphiphilic Creams |
|-------------------|---------------------|-------------|---------------------------------|
| Polymers          |                     | Natural gels:  -Protein gels  -Polysaccharide gels  Synthetic gels:  -Organic polymer gels  -Inorganic gels  Hybrid gels:  -Natural polymers  -Synthetic polymers |

**Table 3-1 (A) Classified based on different solvent phases (B) Classified based on different crosslinkages (C) Classified based on different constituent phases (Taken from Wolfgang Ostwald, 1923) [41]**
Later in 1974 Flory proposed a more common and detailed gel classification. Based on the structural criteria, gels were classified into four types: (1) Gels with well-ordered lamellar structures, (2) Gels with covalent polymeric networks, (3) Gels with polymer networks formed through physical aggregation, (4) Gels with particulate disordered structures. [42] His work indicated that the crosslinking of molecular units form a 3D network through covalent or non-covalent interactions, which is crucial for the elasticity of gel. Gels with the crosslinking region formed by covalent interactions are generally recognized as chemical gels, while physical gels are formed by non-covalent interactions, such as hydrogen-bonding, [22-24] pi-pi stacking, [25] dipole-dipole interactions, [26, 27] and London dispersion forces. [28] However, it has been found out that certain gels contain highly extended fibers arised from entanglements instead of a cross-linked network. There are no strong evidence that can prove that cross-links apply in all gels. [43] In a nutshell, the classification of gels is described in Fig. 3.1 according to different criteria, such as the source, the crosslinking type, the constitution, and the medium of gels. [44, 45]
3.2 Organogels

3.2.1 Introduction:

Over the last decade, the study of organogels has become an active field of research due to their wide range of applications, such as recovery of oil spills, [10] controlled drug release, [20] light harvesting. [21] Although organogels have features and mechanical properties of a solid, they are mainly comprised of organic solvents. Two further categories of organogels are molecular gels and polymeric gels based on the size of the gelator.[36, 46, 47] Molecular gels are comprised of low molecular weight organogelators (LMOGs) which have a molecular weight less than 2000 Daltons, whereas, polymeric gels are formed with larger size macromolecules. [36, 47, 48] Due to the structuring effect of organogelators, many of them are found to be
alternative oil structuring agents, such as mono- and diglycerides, fatty acids, fatty alcohols, waxes, phospholipids, sorbitan esters, phytosterols, etc. [29] The structuring process of these organogelators vary widely depending on the different building blocks shown in Table 3.2.

<table>
<thead>
<tr>
<th>Categories</th>
<th>Organogelator</th>
<th>Mechanism of the network</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline Particles</td>
<td>Diacylglycerols, monoacylglycerols, fatty acids, wax esters, ceramides</td>
<td>Colloidal crystalline triacylglycerol particles that trap the liquid TAG phase inside, thus causing gelling</td>
</tr>
<tr>
<td>Self-assembled Fibrillar Network (SAFiN)</td>
<td>Phytosterols with oryzanol, ricinoleic acid, 12-HSA</td>
<td>Crystalline fibers twisted and entangled forming a three-dimensional network.</td>
</tr>
<tr>
<td>Polymeric Strands</td>
<td>Cellulose, starch, gelatin</td>
<td>Cross-linked network stabilized by covalent or non-covalent bond</td>
</tr>
<tr>
<td>Particle-filled Networks</td>
<td>A solid or a liquid inert particles</td>
<td>The high concentration of particles exceed the close packing faction which allows mechanical contact between particles forming the network</td>
</tr>
<tr>
<td>Liquid Crystalline Mesophases</td>
<td>Monoacylglycerol</td>
<td>The formation of semi crystalline scaffolds which can trap oil</td>
</tr>
</tbody>
</table>

Table 3-2 Building blocks for the formation of the three dimensional network in structured oils. (Taken from Marangoni and Garti, 2011) [2]
3.2.2 Molecular gels

3.2.2.1 Introduction

Unlike polymeric gels, of which the gelators are macromolecular, molecular gels are formed by LMOGs. [16, 45] The 3D network of molecular gels are formed through self-aggregation of the LMOGs and they are thermally reversible due to the weak non-covalent interactions stabilizing their supramolecular structures. [36, 45, 49] With respect to their rheological behavior, molecular gels are solid-like materials with a storage modulus (G’) greater than their loss modulus (G’) over a wide range of frequency within the linear viscoelastic region. [36, 50] Generally a molecular gel is prepared by heating the mixture of LMOGs and organic solvent over the LMOGs’ melting point and then cooled, leading to a supersaturated solution. [14, 49] The super saturation is the driving force for the self-assembly of the LMOGs into a SAFiN, which is held together by a balance of gelator-solvent interactions. [13-16, 49] The intermolecular interactions in molecular gels are often found as a combination of non-covalent interactions, such as hydrogen-bonding, [22-24] pi-pi stacking, [25] dipole-dipole interactions, [26, 27] and London dispersion forces. [28]

It has been reported that a precise ratio of gelator-gelator to gelator-solvent interactions is crucial in the formation of a SAFiN structure. [19] In another words, the formation of SAFiNs lies in a strict balance between the solubility and insolubility of the LMOGs in a given solvent. [10] When the gelator-gelator interaction is too strong, meaning the gelator is too insoluble in the given solvent, resulting in phase separation and precipitation. On the contrary, a solution forms when the gelator-solvent interactions are too strong and the gelator is too soluble in the solvent. [10, 16, 19]
3.2.2.2 Low Molecular Weight Organogelators (LMOGs)

LMOGs are gelators with a molecular weight less than 2000 Da, which are able to constrain organic solvents through a self-assembled 3D network.[36, 45, 49] The LMOGs can be classified into various categories based on their different molecular structures. From the simplest alkanes to the complicated phthalocyanines, numerous gelators have been discovered in the last decade. [36, 45] Several classes of LMOGs are illustrated in Fig.3.2. [45]

Figure 3-2 Several different classes of LMOGs (Taken from Neralagatta M. et al., 2005) [45]
Due to the differences among the structure of the LMOGs, the associated intermolecular interactions vary (e.g., compared with alkanes, the LMOGs of alkanoic acid can stabilize their aggregates not only by London dispersion forces but also H-bonding interactions). [51, 52] As mentioned before, the weak physical interactions, which control the self-assembly of LMOGs, are hydrogen-bonding, [22-24] pi-pi stacking, [25] dipole-dipole interactions, [26, 27] and London dispersion forces etc. [28] By modifying the structure of the LMOGs, (e.g., adding certain functional groups), favorable intermolecular interactions which are associated with desired properties of the LMOGs can be obtained. [52] In the mean time, the understanding of the intermolecular interactions that control the development of entangled network is important for the design of LMOGs as well. (Fig.3.3) [53]

Figure 3-3 Schematic view of gelation of organic solvents by small organic molecules (Taken from V. Balzani et al., 1999)[53]
3.2.2.3 Self-Assemble Fibrillar Networks (SAFiNs)

The history of SAFiNs from molecular gels formed by LMOGs through physical non-covalent interactions may go back to the middle of the 20th century. [54] In the last decade, the discovery and design of the LMOGs and their SAFiNs have experienced increasing interests due to a wide range of applications. [2, 10, 45, 55-57] It has been reported that the formation of 3D network of SAFiNs is first initiated by molecular level recognition of the LMOGs, resulting in one-dimensional (1D) objects such as fibers, stands, tapes or tubules, then undergo further interactions at junction zones to form 3D networks. [51, 54, 58, 59] The primary, secondary, and tertiary structure of a molecular gel is illustrated by Lara A. Estroff et al. (Fig. 3.4). [58]

![Diagram of molecular gel structure](image)

*Figure 3-4 The primary, secondary, and tertiary structure of a self assembled physical gel molecules (Taken from Lara A. Estroff et al., 2003)[58]*
The primary structure is formed by 0D objects (i.e., small aggregates of LMOGs), which is determined by the molecular level recognition. [58] The secondary structure is formed as the morphology of the aggregates such as, micelles, vesicles, fibers, ribbons, etc., which are also known as 1D objects. [51, 58] Both of the primary structure and the secondary structures are at the nano- to micrometer scale. [58] Although numerous attempts have been made to explain how and why 0D objects transform into 1D objects, no applicable rules have been found until recently. [54] The mechanism that controls the aggregation of the LMOGs into 1D objects is affected by many factors including the structure of the LMOGs, the solvent nature, and the sol-gel transformation mode. [54] The study of the mechanism of the SAFiNs structure from 0D to 3D objects is elaborated in Fig.3.5. [54, 58]

Figure 3-5 Cartoon representation of the steps in the evolution of LMOGs (0D objects; tear drops) to fibers (1D objects) and, in some cases, to SAFiNs (3-D objects) in liquids (wave lines). (Taken from Xiang Yang Liu et al., 2013)[54]
The initial self-assembly processes that converts LMOGs (0D objects) to fibers (1D objects) is poorly understood compared to the self-assembly of the fibers into the fibrillar networks (3D objects). [54] The interactions that contribute to the formation of SAFINs are the entanglement and fiber branching, which are also known as the distribution of junctions. [54, 59] The junctions are the points where fibers join together creating a 3D network, which include transient junctions and permanent junctions. (Fig.3.6)[59]

![Figure 3-6 Different types of junctions occurring in fibrous networks. (Taken from Jing Liang Li et al., 2006)[59]

Transient junctions are often involved with fiber entanglement or crossover, which are not as strong as the permanent junctions formed through the branching or crystallographic mismatches of fibers. Therefore, SAFINs with permanent junctions
are more effective at immobilizing liquids. Two types of fiber branching have been reported: tip and side branching. The side branching can form fibrous networks either with open loops or closed loops. (Fig. 3.6, Fig. 3.7) [59] The open loop fibrous network (Fig. 3.7b) is also recognized as a ‘Cayley-tree’ network, which form spherulites. Unlike a closed loop fiber network, (Fig. 3.7a) within which the fibers are interlocked and mutually connected, fibers of the spherulites are compact within their own domains. No direct connection is observed between adjacent spherulites. [59] Due to the poor contact among the individual spherulites, the elastic nature of the network is very weak. [59] Gels with spherulitic microstructure tend to form opaque gels with high critical gelator concentration. [13]

Figure 3-7 Illustration of side branching fiber network. a) Closed loop fiber network. b) Open loop fiber network (left), and spherulite as a typical Cayley tree-like network (right). (Taken from Jing Liang Li et al., 2006)[59]
3.2.2.4 Nucleation

Nucleation is the starting point for forming a new phase from a solution. [36, 60, 61] As mentioned before, the SAFiNs structure of molecular gels are formed from 0D object to 1D and eventually 3D objects. [54, 58] The process of transforming 0D to 1D object involves nucleation also known as molecular self-recognition of the gelator molecules. [54] Molecular gels are often prepared by cooling the fully melted gelator and solvent mixture, which creates a supersaturation solution. Supersaturation is the driving force for molecular gel nucleation, which can be thermodynamically defined as the difference between the Gibbs free energy (G) values in both solid and liquid phase. [36, 62] As a spontaneous process, nucleation leads to the formation of a new phase corresponding with a lower Gibbs free energy (G). [36] The change of the Gibbs free energy can be described as the following equation: [36, 63]

\[
\Delta G = -n_\alpha \Delta \mu + \sigma A
\]  
(Equation 3-1)

where \( \sigma \) is the surface tension of the new surface area A, \( \Delta \mu \) is a measure of supersaturation and \( n_\alpha \) is the number of particles in the cluster of the new phase. The very first cluster or nucleus that is responsible for the formation of the rudimentary crystal is termed as the critical cluster or critical nucleus. [36, 60] For homogeneous nucleation, the critical cluster or nucleus determines the minimum size of a cluster or nucleus for a crystal to grow. [60] As the aggregation of the gelator molecules is a result of stochastic processes, the cluster radius (R) is crucial in determining the crystal growth. If the cluster radius (R) is bigger than the critical cluster radius (R_c), the cluster will grow. On the contrary, if R is smaller than R_c, the cluster is likely to dissolve again. (Fig. 3.8) [36] However, no accurate measurements can be made to determine the actual size of the nucleus or cluster.
The number of critical clusters formed per unit time in a unit volume, in other words, the nucleation rate, can be expressed by an Arrhenius-type equation: [36, 61]

\[ J = J_o \exp \left( -\frac{\Delta G_c}{k_B T} \right) \]  

(Equation 3-2)

where \( J_o \) is the pre-exponential factor depending on the supersaturation, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature and \( \Delta G_c \) is the energy barrier to achieve the critical cluster. [36, 61]

![Figure 3-8 The work of cluster formation, W (or the thermodynamic potential \( \Delta G \)) in the formation of a new phase (left). The heterogeneous nucleus formation on a foreign substrate (right). (Taken from Jing-Liang Li and Xiang-Yang Liu) [59]

Apparently, the new phase formation cannot solely rely on the cluster size. Many other factors, such as the density of the cluster and the system composition also affect the phase formation. [36, 60]

When foreign particles are present in the system, heterogeneous nucleation occurs. [60] The heterogeneous centers provide surface for nucleus, which reduces the surface area of the critical nucleus. (Fig. 3.8) [59] In this way, the work to achieve the
critical nucleus formation ($W_c$) is reduced resulting in faster nucleation. The relationship between the work of critical homogeneous nucleus formation ($W_c^{(hom)}$) and the work of critical heterogeneous nucleus formation ($W_c^{(het)}$) can be described in the following equation: [36]

$$W_c^{het} = W_c^{hom} \varphi, \varphi \leq 1 \quad \text{(Equation 3-2)}$$

where $\varphi$ is determined by the heterogeneous nucleation cores, which lowered the nucleation barrier for the formation of the new phase in the system. (Fig. 3.8) [36, 64]

In most cases, foreign particles such as air bubbles, dust, container surface, which serve as nucleation sites, cannot be avoided. [36, 59, 60] However, not all foreign particles are considered active for nucleation. [36]

3.2.2.5 Crystal Growth

In general, crystal growth involves a series of processes: [61] 1) atoms travel through solution; 2) atoms adhere to the surface; 3) atoms change location on the surface; and 4) atoms adhere to edges and kinks. The size of the crystal increases leading to a macroscopic crystalline structure. In molecular gels, the crystalline fibers grow in two different ways depending on their structural match between the nucleus and the substrate. (Fig. 3.9) [59] A good interfacial structural match happens when the new atoms on the growing crystal organize in the same pattern as their parent crystal, which gives rise to a long crystalline fiber. [59, 61] However, a mismatch of crystallographic orientation between the new layers and their parent crystals are often favored resulting in a branched fiber morphology in molecular gels. (Fig. 3.6, Fig. 3.7) [59]
Figure 3-9 Good structural match ($m_1$) between the nucleus and the substrate (A), poor structural match ($m_2$) between the nucleus and the substrate (B). $m_1 > m_2$. (Taken from Jing-Liang Li and Xiang-Yang Liu) [59]

The crystallographic mismatch branching (CMB) mechanism has been supported by many studies. [22, 65, 66] According to the CMB mechanism, there are two major branching systems: tip branching and side branching, as shown in Fig. 3.6. [59] Tip branching happens when the system is under a high degree of supersaturation, whereas side branching occurs at a relatively low supersaturation. [59]

3.2.3 12-Hydroxystearic Acid (12HSA)

Among the broad range of organogelators, which may have potential in the food industry, 12-hydroxystearic acid (12HSA) is of special interest. [36, 51, 67] 12HSA is an ideal gelator, which is not only efficient in gelating a variety of organic liquids, but also less toxic compared with other LMOGs. [36, 67] The commercially available 12HSA is a hydroxylated fatty acid with a 18-C backbone obtained from castor oil. (Fig.3.10) [67, 68] With hydroxyl groups at C-12 positions, the chiral carbon, 12HSA are able to form unidirectional hydrogen bonding, which grows 1-dimensionally resulting in fiber formation. (Fig.3.11) [12, 51]
Figure 3-10 Numbering of atoms and conformation of DL-12-hydroxystearic acid. (Taken from Tetsuro Kuwahara et al., 1996) [68]

The hydrogen bond sequence along the α-axis formed by the hydroxyl groups at C-12 position is illustrated in Fig. 3.12. [12, 68] The angle of C_{12}-O_3-O_3 is 117° and the distance between the adjacent O_3 atoms is 2.87 Å. [24] It has been reported that the packing of stearic acid is similar to 12HSA. [24] However, stearic acid is not as efficient as 12HSA in gelating solvents. [51] The bond angle of C_{10}-C_{11}-C_{12}-C_{13} of 12-HSA deviate from 180° to 173° due to the hydroxyl group at C-12 position resulting in the bend of the molecular structure. [24] It is believed that such bending structure can fill up the space of the extended hydrogen-bonding network.

Figure 3-11 Structural model of the (R)-12-HSA fibrillar or ribbon-like aggregates in organic solvents with the parallel vertical lines representing the direction of the H-bonding network. (Taken from Richard G. Weiss et al., 2006) [36, 51]
Furthermore, according to the calculated density, 12HSA (1.052 g/cm$^3$) can form a more packed structure than stearic acid (1.044 g/cm$^3$). Therefore, the secondary H-bonding networks of the hydroxyl groups at the C-12 position promotes its gelation behavior. [51]

3.3 Solubility Parameters

3.3.1 Introduction

Solubility parameters have been found to be a useful tool in the selection of solvents for polymers in the coating industry. [69, 70] The simplest principle “like dissolves like” indicating that molecules with similar solubility parameters share high affinity for each other. [69] Therefore, the solubility parameters are used to predict if one compound can dissolve in another. Recently, solubility parameters developed for polymers have been applied to molecular gels. [14, 30] With only a few exceptions, Raynal and Bouteiler first proved that the samples gelled by a large array of LMOGs had similar Hanson solubility parameters (HSP) of their solvents. [71] Later, strong correlations found between hydrogen-bonding Hanson solubility parameter ($\delta_h$) and
gel formation, for 12HSA, where: \( \delta_h < 4.7 \text{ MPa}^{1/2} \) forms a clear gel, \( 4.7 < \delta_h < 6.5 \text{ MPa}^{1/2} \) results in opaque gels or precipitate gels, and when \( \delta_h > 6.5 \text{ MPa}^{1/2} \) it remains a solution. [14] It is well known that the formation of a molecular gel depends on a balanced gelator-gelator and gelator-solvent interactions. [14, 72] Therefore, not only the solvents’ solubility parameters need to be taken into consideration, but also the gelators’ as well. [71] Even though there is a lack of information towards the untested LMOGs and organics solvents, the prediction ability of solubility parameters is so far very promising.

3.3.2 Hildebrand Solubility Parameters

The definition of Hildebrand Solubility Parameters is often known as the square root of the cohesive energy density: [69]

\[
\delta = \left( \frac{E}{V} \right)^{1/2} \tag{Equation 3-1}
\]

where \( E \) represents the energy of vaporization, which is defined as the energy needed to convert a molecule from the liquid phase to the gaseous phase, \( V \) is the molar volume of the pure solvent. [69] Therefore, the energy required to evaporate a volume unit of liquid is recognized as the cohesive energy density (CED). [73] According to the International System of Units (SI), the unit of solubility parameters is MPa^{1/2}. The spontaneous solution process occur when the free energy of mixing equal to or blew zero, which is governed by the free energy of mixing: [69, 74]

\[
\Delta G^M = \Delta H^M - T\Delta S^M \tag{Equation 3-2}
\]

where \( \Delta G^M \) is the Gibbs’ free energy of mixing, \( \Delta H^M \) is the change of the enthalpy on mixing, \( T \) is the absolute temperature, and \( \Delta S^M \) is the entropy change of mixing. The \( T\Delta S^M \) is positive as the mixing process is in favor of the increase in entropy. The calculation of \( \Delta H^M \) proposed by Hildebrand and Scott is listed as: [69]
\[ \Delta H^M = \varphi_1 \varphi_2 V_M (\delta_1 - \delta_2)^2 \] (Equation 3-2)

where \( \varphi_1 \) and \( \varphi_2 \) represent the volume fractions of the components for solvent and polymer, and \( V_M \) is the total volume of the mixture. However, equation 3-2 has been proved wrong as the heat of mixing is not always positive. [69, 74] Still this theory has found very useful since there are not too many exceptions in the polymer solutions. Another shortcoming with the Hildebrand Solubility Parameters has been reported that its application is limited to nonpolar compounds only where dipole-dipole interactions are predominant.[69, 75] Thus, Hildebrand Solubility Parameters is inaccurate to work with polar compounds where polar interactions and hydrogen bonding interactions are also important. [74]

3.3.3 Hansen Solubility Parameters (HSPs)

3.3.3.1 Introduction

Hansen solubility parameters (HSPs) also known as the three dimensional solubility parameters, which is so far the most promising technique in predicting polymer solubility. [69] It has been assumed that the total cohesive energy \( (E_T) \) can be decomposed into three major modes of contributions: dispersion forces \( (E_D) \), polar forces \( (E_P) \), and hydrogen bonding forces \( (E_H) \). [69] Their relationship can be described as: [69]

\[ E_T = E_D + E_P + E_H \] (Equation 3-3)

By dividing the total cohesive energy \( (E_T) \) and each individual energies \( (E_D, E_P, E_H) \) by the molar volume \( (V) \), the squares of total Hansen solubility parameters \( (\delta_T) \), and each individual Hansen solubility parameters \( (\delta_D, \delta_P, \delta_H) \) can be obtained: [69]

\[ E_T / V = E_D / V + E_P / V + E_H / V \] (Equation 3-4)

\[ \delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \] (Equation 3-5)
In this approach, the affinity for different materials cannot be determined only by the \( \delta_t \), the individual Hansen solubility parameters: dispersion Hansen solubility parameters (\( \delta_d \)), polar Hansen solubility parameters (\( \delta_p \)), and hydrogen bonding Hansen solubility parameters (\( \delta_h \)) should also be put into consideration. [69]

3.3.3.2 Group Contribution Methods (GCMs)

Group contribution methods (GCMs) are widely used to acquire an estimation of HSPs for a broad range of organic compounds with complex structures. [14, 76, 77] By subdividing the compounds into functional groups, of which the atomic and group increments are additive, one can easily calculate the HSPs. [14, 76, 78] One of the existing group contribution methods established by Hoftyzer and Van Krevelen for estimating the solubility parameters are illustrated as the following equations: [76, 79]

\[
\delta_d = \frac{\Sigma F_{di}}{V} \quad \text{(Equation 3-6)}
\]

\[
\delta_p = \sqrt{\frac{\Sigma F_{pi}^2}{V}} \quad \text{(Equation 3-7)}
\]

\[
\delta_d = \sqrt{\frac{\Sigma F_{hi}}{V}} \quad \text{(Equation 3-8)}
\]

where \( F_{di} \), \( F_{pi} \), \( F_{hi} \) represent the dispersive component, polar component and hydrogen bonding component of the group contribution respectively, and \( V \) is the molar volume. [14]

3.3.3.3 Hansen Space

The three individual Hansen solubility parameters (\( \delta_d \), \( \delta_p \), \( \delta_h \)) can be used as coordinates to locate a point in a 3D space known as the Hansen space. [14, 69, 71] The values of HSPs for each solvent and solute can be found in the literature or calculated. [14, 71] The distance between two points in Hansen space can be calculated in the following equation: [69]
\[(Ra)^2 = 4(\delta_{d2} - \delta_{d1})^2 + 4(\delta_{p2} - \delta_{p1})^2 + 4(\delta_{h2} - \delta_{h1})^2 \]  
(Equation 3-9)

where \(Ra\) is the distance, \((\delta_{d1}, \delta_{p1}, \delta_{h1})\) and \((\delta_{d2}, \delta_{p2}, \delta_{h2})\) are the individual HSPs of two materials. According to a set of extensive solubility data, it has been found that the closer the two points are in the Hansen space, the more likely of being miscible for the two materials. [69, 71] The solubility sphere is defined as the region in which the good solvents for a specific solute all group together. (Fig.3.13) [69, 80]

As mentioned before, HSPs can be used to predict the gelation behavior in the field of molecular gels. [14, 71] Thus, one cannot only define a solubility sphere but also a gelation sphere and a precipitate sphere for a specific gelator in Hansen space. (Fig.3.14) [31]
Figure 3-14 Solubility data for Pyrenyl-Linker-Glucono in liquid mixtures represented in Hansen space: solubility sphere (blue), gel sphere (green), and precipitate sphere (red). (Taken from Ni Yan et al., 2013) [31]

By identifying the location of an untested solvent in the Hansen space for a given gelator, one can predict if the gelator can gel the solvent or not.[71]

3.4 References


41. Ostwald, W., Practical Colloid Chemistry. 1923.


4.0 Self-Assembly of 12-Hydroxystearic Acid Molecular Gels in Mixed Solvent Systems Rationalized using Hansen Solubility Parameters

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**This chapter is published in Colloid and Polymer Science, 2015, 293, 975-983.

(DOI:10.1007/s00396-014-3480-9) Published: Dec 11, 2014.
4.1 Abstract

Recent advances in understanding the underlying mechanisms of self-assembly in molecular gels using Hansen solubility parameters (HSPs) have focused on gelator-single solvent mixtures. Linear correlations between critical gelator concentration (CGC) and polar HSP formed in specific regions where each region has the same proportion of octane with different ratios of either 1-octanol and 1-octylamine. CGC increases with an increasing proportion of 1-octanol and a decreasing proportion of 1-octylamine as the polar HSP increases within each region. Both G' and breaking points decrease in a log-linear fashion as each individual HSP or total HSP increases, suggesting that 1-octanol-rich gels do not form strong gels because of hydrogen-bonding between 1-octanol and 12-HSA which is capable of impeding fiber growth. The interaction between 12-HSA and 1-octanol is more disruptive to fiber growth than 1-octylamine which arises because of the solvents ability to accept or donate a hydrogen-bond.

4.2 Introduction

Molecular gels, comprised of low molecular weight organogelators (LMOGs), are thermally-reversible, semi-solid materials where the solvent is immobilized on a macroscopic scale by the three-dimensional (3D) self-assembled fibrillar network (SAFiN). [1-3] LMOGs aggregate onto the SAFiN by physical, non-covalent interactions including: hydrogen-bonding, [4-7] pi-pi stacking, [8] dipole-dipole interactions, [9, 10] and London dispersion forces. [11] A precise balance between gelator-gelator interactions and gelator-solvent interactions is required for SAFiN formation; excessive gelator-gelator interactions interfere with unidirectional fibrillar growth leading to thicker fibers and eventually impede fibrous structures from forming. [12, 13] LMOGs have become a major topic of interest over the past decade.

The capacity of LMOGs to result in SAFiNs, and ultimately molecular gels, has been widely studied. [18-20] Numerous attempts to correlate solvent parameters to gelation have been met with mixed success. Bielejewski et al. showed that the hydrogen-bonding network of 1,2-O-(1-ethylpropyldene)-α-D-glucofuranos and their thermal stability were both affected by solvent polarity. [21] Later, solvent chemistry was tailored using ethanol as a co-solvent with toluene to control polarity and hydrogen bonding interactions of diphenylalanine (L-Phe-L-Phe, FF). [22] Of the solvent parameters studied, Hansen solubility parameters (HSPs), which consists of dispersive interactions ($\delta_d$), polar interactions ($\delta_p$), and hydrogen-bonding interactions ($\delta_h$), have been the most useful at predicting 12HSA gelation ability and it appears that $\delta_h$ correlates most strongly with gelation ability and solvent chemistry. [1, 13, 18, 23-29] It is has been shown that the $\delta_h$ has a positive linear correlation with critical gelation concentration (CGC) for 12HSA. [12, 13]

The majority of research with regards to HSPs and molecule gels has focused on a gelator mixed in a single solvent. To date, only a handful of studies have been completed on a mixed dual solvent systems using HSPs. [27, 30-33] One such study included the properties of Pyrenyl-Linker-Glucono gelators in tetrahydrofuran-water mixtures were examined. [30] They found the composition of the liquid mixtures had an effect on the solubility, gelation ability, crystallite size, CGC, microstructure, thermal and mechanical stabilities of the gels, etc. [30] The likelihood of gel
formation depends on the HSPs of gelator and solvent combinations; the rheological properties of the gel illustrate the importance of the hydrogen-bonding interactions and mechanical stability. [30] Strong correlations found between δₜ and gel formation, for 12HSA, where: δₜ < 4.7 MPaⁱ/₂ forms a clear gel, 4.7 < δₜ < 6.5 MPaⁱ/₂ results in opaque gels or precipitate gels, and when δₜ > 6.5 MPaⁱ/₂ it remains a solution. [13] The hydrogen bonding HSP seems to be a more predictive parameter than other solvent polarity measures for determining gelation behaviors for 1,3:2,4-dibenzylidene sorbitol (DBS). [34]

12HSA molecular gels have two different polymorphic forms depending on the solvent employed to make the gel; hexagonal subcells (~4.1 Å) in non-polar (alkanes and thiols) and triclinic parallel subcells (~4.6, 3.9, and 3.8 Å), in polar solvents (nitriles, aldehydes, and ketones). [24] The hexagonal polymorphic form corresponded to the SAFiN with CGC less than 1 wt%. The triclinic polymorphic form corresponds to a less effective sphererulite supramolecular crystalline network and a corresponding CGC greater than 1.5 wt%. [24] In this study, the effect of ternary solvent mixtures using—octane, 1-octanol and 1-octylamine—were employed at different ratios to investigate the effects on structure, thermal and rheological properties of a 12HSA/solvent blend.

4.3 Methods

4.3.1 Materials and gel preparation

Octane, 1-octanol, 1-octylamine and 12HSA were obtained from Sigma-Aldrich (St. Louis, MO) with purities greater than 0.95% and were used without further purification. The solvents were selected because 12HSA in octane, forms a
transparent gel, in 1-octylamine 12HSA forms an opaque gel or a precipitate gel and 12HSA in 1-octanol remains a solution at concentrations as high as 5 wt%. [1, 13, 24, 25] Using a ternary phase diagram, and varying the solvent ratio in 10% increments, generated 66 solvent combinations. Initially, 1 g sample with 3 wt% 12-HSA/solvent was prepared in 8 ml vials. Samples were heated to 100°C for 20 min and stored for 24 hrs at 25 °C. The tube inversion method was used to determine if it was a gel; upon inverting the vial for 1 hour if no flow was observed under its own weight then the sample was classified crudely as a gel. If no flow was observed, the sample was diluted in by 0.5%, reheated to 100 °C and cooled to 25 °C and re-tested until flow was observed, the last concentration that impeded flow was noted to be the CGC.

4.3.2 Polarized light microscopy

Polarized light micrographs were obtained for each 3 wt% 12HSA gels in each of the 66 solvent combinations using a Linkham imaging station (Linkham, Surrey, England) equipped with a Q imaging 2560×1920 pixel CCD camera (Micropublisher, Surrey, Canada) and a 10X Olympus lens (0.25 N.A.) (Olympus, Tokyo, Japan). Samples were placed on a glass slide and covered by a glass coverslip. All the samples were observed at ~25°C under polarized light.

4.3.3 Rheological measurements

A Discovery hybrid rheometer (TA instruments, New Castle, DE) was used to assess the rheological properties of the gels using an 80 mm flat peltier plate (TA instruments, New Castle, DE). An oscillatory stress sweep at 1 Hz was conducted between 0 and 5000 Pa to determine the linear viscoelastic region (LVR). Samples were prepared in aluminum molds comprised of Swagelok compression fittings, which acted as gas-tight seals to prevent the volatilization of the solvent during
heating. The gels, obtained from the aluminum molds were 8 mm in diameter and 5 mm thick. The yield stress was determined when the G’ decreased from the LVR by 10%.

4.3.4 Differential scanning calorimetry

Differential scanning calorimetry (DSC)(Q2000, TA Instruments, New Castle, DE) was used to determine the melting point of 6 to 10 mg the sample sealed in hermetic aluminum pans (TA Instruments, New Castle, DE). The DSC chamber was maintained at 20°C and flushed with nitrogen (0.5 ml/min). The sample was then heated to 100°C at 2°C/min.

4.4 Results and discussion

Individual HSPs for the solvent combination are calculated using their weight percent distribution:

\[ \delta_x = \sum (\delta_x)_i \phi_i \]  

(Equation 4-1)

where x stands for the dispersive, polar, or hydrogen bonding component of i solvent where i represents octane, 1-octanol or 1-octylamine. \( \phi_i \) is the weight percent of component i in each mixture. [35] The HSP of 12HSA have previously been calculated using the group contribution method. [36-39] Hansen space was used to observe if the different states (i.e., sol, gel or precipitate) of the 3 wt% 12HSA/solvent combinations clustered in different regions (Fig. 4.1). Each of the pure solvents have similar dispersive components (i.e., \( \delta_d \text{ Octane} = 15.5 \text{ MPa}^{1/2} \), \( \delta_d \text{ Octanol} = 17.0 \text{ MPa}^{1/2} \), \( \delta_d \text{ Octylamine} = 15.6 \text{ MPa}^{1/2} \)) therefore it appears as though the points align within the spheres on the Hansen plot (Fig. 4.1). 12HSA precipitates occupied the smallest region of Hansen space, while the gel and solution spheres were similar in size but not location. The center (2\( \delta_d \), \( \delta_p \), \( \delta_h \)) of precipitate sphere is 31.7, 3.5, 8.4 MPa\(^{1/2}\), and the
radius ($R_{pre}$) is 1.94 MPa$^{1/2}$; the center of solution sphere is 31.6, 3.0 and 7.14 MPa$^{1/2}$ and the radius ($R_{sol}$) is 5.18 MPa$^{1/2}$. Finally, the center of gel sphere is 31.4, 2.2 and 5.23 MPa$^{1/2}$ with a radius ($R_{gel}$) of 5.67 MPa$^{1/2}$. However, with this system of solvent, the 3D Hansen space is unable to discern the different sols, gels and precipitates. Thus, we were interested to study if there are any correlations with individual HSPs.

![Figure 4-1: 2D and 3D Hansen space for the different gel, solution and precipitate states of 12HSA/solvent combinations (i.e., octane, 1-octanol, and 1-octylamine). Yellow points represent solutions, blue points gels and orange points precipitates. The blue mesh sphere corresponds to the solutions HSP, and the green mesh sphere to the gel HSP.](image-url)
The HSPs for 12HSA, calculated using the group contribution method ($\delta_d=17.59$ MPa$^{1/2}$, $\delta_p=2.86$ MPa$^{1/2}$, $\delta_h=6.77$ MPa$^{1/2}$ [13]), was used to calculate the distance between 12HSA and the solvent combinations, in Hansen space and were plotted versus the total HSP ($\delta_t$) (Fig. 2A). It is important to note that other methods may be advantageous over determined the Hansen coordinates for 12HSA including the center of the solubility sphere.[27] Bonnet et al., [27] showed that the values for 12HSA, determined using the center of the solubility sphere, differed from the group contribution methods. For $R_{ij}$ calculations, the 12HSA coordinates were calculated using the group contribution mentions (A, C) and the center of the solubility sphere from previous works (B,D). The vector distance ($R_{ij}$) was calculated using the following equation:

$$R_{ij}=(4(\delta_{di}-\delta_{dj})^2+(\delta_{pi}-\delta_{pj})^2+(\delta_{hi}-\delta_{hj})^2)^{1/2} \quad \text{(Equation 4-2)}$$

Below $\delta_t \sim 18.0$ MPa$^{1/2}$ gels formed at lower $\delta_t$ irrespective of the distance between the solvent and gelator and sols remained at higher $\delta_t$ (i.e., the solutions are located on the right side of the distributed data, while gels are concentrated on the left side) (Fig. 4.2A, B). When $\delta_t < 18.0$ MPa$^{1/2}$ no precipitates formed. Above a total HSP of 18.0 MPa$^{1/2}$ the solutions tended to lie on the right side of the data and the sols were not differentiated, in $\delta_t$, from the precipitates (Fig. 4.2A). This explains why $R_{ij}$ is not the only factor in predicting gel behavior and is unable to define clear trends between CGC and $R_{ij}$ (Fig. 4.2C,D).[13] The total HSP, related to the directionality in Hansen space, is crucial in determining organogel formation due to the fact that a strong hydrogen bonding component or polar component may interfere with gelator-gelator interactions resulting in solutions or precipitates.
Figure 4-2: The distance, in Hansen space, between 12HSA, calculated using the group contributions method (A,C) and the center of the solubility sphere (B,D)\textsuperscript{14e} and the mixed solvent systems versus the total Hansen solubility parameter (A,C) and the CGC as a function of the Hansen distance between the mixed solvents and 12HSA (B,D).

In order to better typify the gelation behavior of 12HSA in complex solvent mixtures, the CGC was assessed as a function of each individual HSP and the total HSP (Fig. 4.3). Solvent mixtures that contained a majority of octanol (i.e., above 50 wt\%) (i.e., Fig. 4.3, red square) correspond to the highest CGC values. Previously, it has been shown 12HSA in 1-octanol remains a solution; [13] therefore, the octanol-rich (octanol\textgeq 50\%) solvent mixtures tend to require higher concentrations of 12HSA due to the strong gelator-solvent interaction. Even though 1-octylamine is capable of hydrogen-bonding, the relative strength is lower than 1-octanol and is insufficient to impede fibrillar growth of 12HSA. Therefore, the 1-octylamine-rich gels (i.e., Fig. 4.3, green diamonds) correspond with lower CGC compared with 1-octanol-rich gels (red square). Furthermore, the capacity to donate and accept a hydrogen bond is very
different between these two solvents. HSPiP software dissects the $\delta_h$ into the energy associated with a hydrogen bond donor and acceptor. In the case of 1-octanol, the hydrogen bond donor energy versus acceptor ratio ($\delta_{hD/A}$) is 6.9/8.7; for 1-octylamine the $\delta_{hD/A}$ is 0.1/7.4. Since these solvents have similar energies associated with the acceptance of hydrogen bonds, the solvation of 12HSA in 1-octanol is probably due, in part, to the high hydrogen bond donating energy. Interestingly, several gels rich in octane (octane $\geq$ 50%) also correspond with high CGC. For example, the gel with 90% of octane and 10% of 1-octylamine has a CGC of 2.8 wt% while the CGC of pure octane is only 0.3 wt%. The vast change of CGC shows that small amounts of polar and hydrogen-bonding solvents are capable of disrupting the 12HSA fiber growth. Overall there is no clear isolation among gel, solution and precipitate according to the HSP. However, all of the solutions and precipitates are rich in 1-octanol ($\geq$ 50%) with the exception of three that are solutions rich in 1-octane ($\geq$ 50%).

![Figure 4-3: CGC versus the dispersive component of the HSP (A), the polar component of the HSP (B), the hydrogen-bonding component of the HSP (C) and](image-url)
the total HSP (D). Precipitates are graphically illustrated arbitrarily at 4 wt% and solution are represented at 0 wt%.

Certain regions within $\delta_p$ show linear correlations with CGC. Within each region, where linearity is observed, has the same proportion of octane and varying ratios of both 1-octanol and 1-octylamine (i.e., Region 1, 60% octane, $(1.12 < \delta_p < 1.22 \text{ MPa}^{1/2})$; region 2, 50% octane $(1.4 < \delta_p < 1.55 \text{ MPa}^{1/2})$; region 3, 40% octane $(1.68 < \delta_p < 1.88 \text{ MPa}^{1/2})$, region 4, 30% octane $(1.96 < \delta_p < 2.16 \text{ MPa}^{1/2})$; and region 5, 20% octane $(2.24 < \delta_p < 2.54 \text{ MPa}^{1/2})$). As $\delta_p$ increases within each region, CGC increases with an increasing proportion of 1-octanol and a decreasing proportion of 1-octylamine (Fig. 3B). A meticulous balance between gelator-gelator interactions and gelator-solvent interactions is obtained when $\delta_p = 1.4 \text{ MPa}^{1/2}$, $\delta_h = 3.55 \text{ MPa}^{1/2}$ (octane=50%, octylamine=50%) which requires CGC < 0.4 wt%. As the concentration moves away from this ratio, more gelator is required to gel the solvent mixtures. This trend becomes more evident when the data is plotted onto a ternary contour plot (Fig. 4.4). The CGC gradually increases as the proportion of 1-octanol increases (i.e., shown with a color change from purple to red).
Figure 4-4: 2D ternary contour plot of solvents mixture systems. Blank area represents solutions and precipitates. Color scale represents the critical gelator concentration.

The rheological behavior of 12-HSA/mixed solvent gels is also quantified in terms of the HSPs, which are correlated with storage modulus (\(G'\)) (Fig. 4.5) and yield stress/breaking point (Fig. 4.6). The yield stress was experimentally defined as the stress where \(G'\) deviates by 10% from the average \(G'\) obtained within the LVR. Gels rich in 1-octanol correlated to lower \(G'\) and yield stresses compared with octane-rich or 1-octylamine-rich solvents. This matches with the previous findings that 12HSA in 1-octanol remains a solution and the gels rich in 1-octanol correspond with high CGC.

[13] As each individual HSP or total HSP increases, both \(G'\) and breaking points decrease in a log-linear fashion, suggesting that 1-octanol-rich gels do not form strong gels because of hydrogen-bonding between 1-octanol and 12-HSA which impedes fiber growth.
Figure 4-5: Storage modulus ($G'$) versus the dispersive component of the HSP (A), the polar component of the HSP (B), the hydrogen-bonding component of the HSP (C) and the total HSP (D).
Figure 4-6 Breaking point versus the dispersive component of the HSP (A), the polar component of the HSP (B), the hydrogen-bonding component of the HSP (C) and the total HSP (D).

To further probe the effects of mixed solvents on gelation ability of 12-HSA, the onset temperature of melting, as a function of each individual HSP, total HSP and CGC, was plotted (Fig. 4.7). There is no obvious trends found between melting temperature and solubility parameters nor between melting temperature and CGC. 12HSA in pure octane is not represented on these figures because it skews the axis as it is the only system that melts above 60 °C. However, the five data points that have a melting temperature above 45 °C all have octane concentration equal to, or greater than the concentration of both 1-octanol and 1-octylamine.
Fig. 4-7 Melting temperature as a function of the dispersive component $\delta_d$ (A), the polar component $\delta_p$ (B), the hydrogen-bonding component $\delta_h$ (C), the total HSP $\delta_t$ (D) and the CGC (E).

It is obvious that the melting temperature drops significantly when the solvent changes from a pure octane to a solvent mixture (Fig. 4.8). When octane was blended with 1-octanol and/or 1-octylamine, the melting temperature dropped to between 52.83 °C and 32.12 °C indicating that the crystal size is decreased and/or that more imperfect crystals are present, which associated with an increase in the surface area of
the crystalline structure of the molecular gel. [1] This can be explained by using Gibbs free-energy curves. [40]

Figure: 4-8 2D ternary contour plot of solvents mixture concentration. Blank area represents solutions and precipitates.

For the samples that remained as solutions, no fibers or spherulites were found, only a few small aggregates (Fig. 4.11 bottom right). The macroscopic precipitates are visually represented with images from the supernatant and precipitate as shown in the lower right side of Figure 4.11. It is obvious that the morphology of the samples vary with changing solvent blends, which accounts for the changes in melting temperature and rheological properties.

For the 50 gelled samples with the three solvents mixing at all possible ratios, only pure octane formed a transparent gel with a concentration of 12HSA at 3 wt%. No obvious fiber network structure was found under polarized light due to the fact the long and thin fiber morphology is too fine to be observed as shown in lower left corner.
of Fig 4.11. The rest of the gelled samples are all opaque gels with a fiber morphology. (Fig. 4.11) This result is consistent with the findings from previous research that hydrogen-bonding interactions between solvent and gelator can interfere with the gelator-gelator interactions resulting in thicker fibers.[13, 41]

Figure: 4-9 DSC melting temperature. Octane ratio is constant within each image and identified on top left corner. (A-K) The ratios of 1-octanol decrease and the ratios of 1-octylamine increase from bottom to top within each image at 10% increments.
The onset temperature of melting of gelled samples are illustrated in Figure 4.9 A-K with constant octane ratios in each image. The gelled sample with pure octane has the highest melting point of 64.85°C. (Fig. 4.9A) The melting temperature drops significantly when the liquid composition changes from the pure octane to binary solvent mixture. (Fig. 4.9B) [90% octane with 10% 1-octanol (T$_m$=36.38°C), 90% octane with 10% 1-octylamine (T$_m$=36.52°C)]. This is associated with the change of fiber morphology shown in Figure 4.11 that both of the binary samples formed large aggregates with thick fibers. When 80% octane was mixed with 10% 1-octanol and 10% 1-octylamine, the melting point increased to 52.83°C. (Fig. 4.9C bottom line) The fine and thin fiber morphology was observed at this ratio. (Fig. 4.11) The binary solvent mixture of 80% octane and 20% 1-octylamine formed a coarse fiber morphology with T$_m$ decreasing to 39.21°C. (Fig. 4.9C top line) The same pattern occurred in the three samples with the constant ratio of octane at 70%. A relatively high melting temperature of 48.6°C (Fig. 4.9D bottom line) and fine fiber morphology (Fig. 4.11) were obtained when 70% of octane mixed with 20% of 1-octanol and 10% of 1-octylamine. The melting temperature decreased to 37.51°C and 39.21°C when the ratio of 1-octanol changed to 10% and 0% respectively. (Fig. 4.9D middle and top line) The average melting point of the samples with the constant ratio of octane at 60% is 41.71°C with the maximum T$_m$ of 50.3°C obtained at 10% of 1-octanol with 30% of 1-octylamine. (Fig. 4.9E) Thin and fine fiber morphology was also observed at this point. (Fig. 4.11) The average melting points of the gelled samples with the constant ratio of octane equal to or below 50% dropped to a range between 38.26°C and 36.32°C (Fig. 4.9F-K) [50% octane, average T$_m$=38.056°C, maximum T$_m$=42°C (30% 1-octanol with 20% 1-octylamin), 40% octane, average T$_m$=36.32°C, maximum T$_m$=41.89°C (10% 1-octanol with 50% 1-octylamin), 30% octane, average
$T_m = 37.29^\circ C$, maximum $T_m = 41.50^\circ C$ (10% 1-octanol with 60% 1-octylamin), 20% octane, average $T_m = 37.11^\circ C$, maximum $T_m = 42.49^\circ C$ (10% 1-octanol with 70% 1-octylamin), 10% octane, average $T_m = 38.26^\circ C$, maximum $T_m = 41.41^\circ C$ (60% 1-octanol with 30% 1-octylamin), 0% octane, average $T_m = 37.375^\circ C$, maximum $T_m = 39.37^\circ C$ (20% 1-octanol with 80% 1-octylamin)] suggesting that octane in the mixed solvent system plays a role in maintaining crystal size and/or crystal perfection.

Figure: 4-10 Breaking Point and $G'$. Octane ratios from 0% to 100% are marked with different symbols. $G'$ (Pa) values are illustrated in the upper part and Breaking Points (Pa) are illustrated in the lower part. (A) All gelled samples are numbered (B) and the numbers are used as x axis values for graph A.
Certain patterns were found in Fig. 4.10A, when breaking point and $G'$ were plotted versus the series number from 1 to 50 which represent all possible ratios of solvent mixture at 10% increments shown in Fig. 4.10B. Samples are also grouped based on octane ratios and marked with different symbols. Within each group the octane ratio remains constant and the ratios of 1-octanol decrease and the ratios of 1-octylamine increase as the numbers grow from low to high. Overall the breaking point and $G'$ value increase first and decrease later on as the number increases within each group. In other words, when octane ratio is constant within each group, the $G'$ and breaking point increase with an increasing proportion of 1-octylamine and decreasing proportion of 1-octanol. Even though the $G'$ and breaking point values drop back down after they reach certain point, they still maintain a higher level compared with the starting points within each group. (Fig. 4.10A) This is consistent with the aforementioned result that the gels rich in 1-octanol do not form strong gels due to the strong hydrogen-bonding interaction between 1-octanol and the gelator. However, a certain level of 1-octanol is needed to maintain the rigidity. As is shown in Fig. 4.10A, the highest $G'$ values are achieved at certain ratios of 1-octanol and 1-octylamine in the groups with the constant octane ratios at 60%, 50%, 30%, 20%, 10% and 0% [60% octane with 20% 1-octanol and 20% 1-octylamine, ($G'_{\text{max}}=94602 \text{ Pa}$); 50% octane with 10% 1-octanol and 40% 1-octylamine, ($G'_{\text{max}}=79022 \text{ Pa}$); 30% octane with 10% 1-octanol and 60% 1-octylamine, ($G'_{\text{max}}=95625 \text{ Pa}$); 20% octane with 30% 1-octanol and 50% 1-octylamine, ($G'_{\text{max}}=110866 \text{ Pa}$); 10% octane with 30% 1-octanol and 60% 1-octylamine, ($G'_{\text{max}}=61161 \text{ Pa}$); 0% octane with 10% 1-octanol and 90% 1-octylamine, ($G'_{\text{max}}=79022 \text{ Pa}$)]. The highest breaking points are obtained at certain ratios of 1-octanol and 1-octylamine in the groups with constant octane ratios at 70%, 50%, 40%, 30%, 20%, 10% and 0% [70% octane with 10% octanol and 20%
octylamine, (maximum breaking point=68Pa); 50% octane with 10% octanol and 40% octylamine, (maximum breaking point=28Pa); 40% octane with 10% octanol and 50% octylamine, (maximum breaking point=21Pa); 30% octane with 10% octanol and 60% octylamine, (maximum breaking point=48Pa); 20% octane with 20% octanol and 60% octylamine, (maximum breaking point=39Pa); 10% octane with 30% octanol and 60% octylamine, (maximum breaking point=31Pa); 0% octane with 10% octanol and 90% octylamine, (maximum breaking point=61Pa).

When 90% octane was mixed with 10% 1-octylamine large aggregates of thick fibers were formed. As the 1-octylamine ratio increased from 10% to 50% ($15.69 \leq \delta_1 \leq 16.44 \text{ MPa}^{1/2}$), the size of the aggregates decreased and the number of the aggregates increased. Beyond 50% 1-octylamine ($16.63 \leq \delta_1 \leq 17.37 \text{ MPa}^{1/2}$), the size of aggregates increased resulting in thick fibers. This result correlates with observations made in the changes to the CGC. At low CGC, the crystal morphology maintains large aspect ratio with thin fibers. In binary mixtures of 1-octanol and octane, at 10% 1-octanol, large aggregates were formed. Beyond 10% 1-octanol ($16.6 \leq \delta_1 \leq 21.01 \text{ MPa}^{1/2}$) in the binary mixtures solutions formed. This again proved that the interaction between 12-HSA and 1-octanol is more disruptive to fiber growth than 1-octylamine which may arise because of the solvents ability to accept or donate a hydrogen bond.
In this work, HSPs have been used to explain, the changes observed in CGC and melting temperatures using thermodynamic arguments based on the crystal size and crystal perfection. These factors clearly play a role in the mechanism of self assembly; however it is important to note that this is not an exhaustive thermodynamic argument. For example, several studies have shown that addition of polar solvent, in our case 1-octanol and 1-octylamine compared to octane, will shift the phase diagram and the liquidus line of the gel between the gelator and solvent.[42, 43] Theoretically, this shift in the liquidus line will have significant effects on the solubility and hence CGC as well as the melting temperature.
4.5 Conclusion:

The idea of designing this experiment on a mixed ternary solvent system provides a better understanding of the solvents effects on the 12HSA gel. Gels rich in 1-octanol (≥ 50%) tend to have a higher CGC compared to gels rich in 1-octylamine (≥ 50%) and gels rich in octane (≥ 50%) due to the strong gelator-solvent interaction. It is clear that the hydrogen-bonding interaction (i.e., donor vs. acceptor) is crucial in determining the 12HSA gel formation. Even though 1-octylamine is capable of hydrogen-bonding, it is less effective in impeding fibrillar growth of 12HSA than 1-octanol. 1-Octanol-rich gels do not form strong gels because of hydrogen bonding between the gelator and solvent which impedes fiber growth.
4.6 References


5.0 CONCLUSIONS

This research has focused on investigating the effect of mixed ternary solvent system (octane, 1-octanol, and 1-octylamine) on the gelation behavior of 12HSA gels. It provides a new perspective for examining the solvent effects by mixing the three solvents with the same aliphatic chain length but different functional groups. Therefore, the experiment can differentiate the role of intermolecular interactions associated with each functional group, such as the hydrogen bonding interactions between hydroxyl group of 1-octanol, and between the amine group of 1-octylamine, in the gelation process. On the other hand, by mixing the three solvents at all possible ratios (at 10% weight increments), we can test the effects of hydrogen bonding interaction quantitatively, instead of solely based on the hydrogen bonding Hansen solubility parameter ($\delta_b$) from literature.

The 66 samples within the ternary system were studied using polarized light microscopy, rheological measurements, and differential scanning calorimetry (DSC) to investigate the structure, thermal, and rheological properties. Overall, samples rich in 1-octanol ($\geq 50\%$) tended to form precipitates, or solutions, or gels with higher CGC values compared with octane rich ($\geq 50\%$) or octylamine rich ($\geq 50\%$) samples. Besides, 1-octanol rich gels do not form strong gels and have large aggregates with thick fibers shown under microscope. This result is consistent with the previous findings that hydrogen-bonding interaction is crucial in determining organogel formation due to the fact that too much hydrogen-bonding interactions between the solvent and gelator may interfere with gelator-gelator interactions. A meticulous balance between gelator-gelator interactions and gelator-solvent interactions is obtained when $\delta_p=1.4\ \text{MPa}^{1/2}$, $\delta_h=3.55\ \text{MPa}^{1/2}$ (octane=50 \%,


octylamine=50 %) which requires CGC<0.4 wt%. Even though 1-octylamine is also capable of hydrogen bonding, the relative strength is not as strong as 1-octanol because of the solvents ability to accept or donate a hydrogen bond. That explains the fact that the interaction between 12HSA and 1-octanol is more disruptive to fiber growth resulting in thick fiber.

This work provides new insights into molecular gels, yet there is more work need to be done, such as choosing different gelator, or different mixed solvent system, to complete the study and provide more valuable input in this area.
APPENDIX 1: Ternary phase diagram (TPD) containing Polarized light micrographs of the 12HSA organogels, precipitates and solutions at each proportion of mixed solvents. The proportion of each point is listed as octane:1-octanol:1-octylamine rations at the lower right corner. Inset separates different states of all samples.
APPENDIX 2: (100% OCTANE:0%1-OCTANOL:0%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 3: (90% OCTANE:10%1-OCTANOL:0%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 4: (90% OCTANE:0%1-OCTANOL:10%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 5: (80% OCTANE:10%1-OCTANOL:10%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 6: (80% OCTANE: 0% OCTANOL: 20% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 7: (70% OCTANE: 20% OCTANOL: 10% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 8: (70\% OCTANE:10\% OCTANOL:20\% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 9: (70\% OCTANE:0\% OCTANOL:30\% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 10: (60% OCTANE:30% OCTANOL:10% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 11: (60% OCTANE:20% OCTANOL:20% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 12: (60% OCTANE: 10% 1-OCTANOL: 30% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 13: (60% OCTANE: 0% 1-OCTANOL: 40% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 14: (50% OCTANE: 40% 1-OCTANOL: 10% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 15: (50% OCTANE: 30% 1-OCTANOL: 20% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 16: (50% OCTANE:20%1-OCTANOL:30%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 17: (50% OCTANE:10%1-OCTANOL:40%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 18: (50% OCTANE: 0% - OCTANOL: 50% - OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 19: (40% OCTANE: 40% - OCTANOL: 20% - OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 20: (40% OCTANE:30%-OCTANOL:30%-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 21: (40% OCTANE:20%-OCTANOL:40%-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 22: (40% OCTANE: 10% 1-OCTANOL: 50% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 23: (40% OCTANE: 0% 1-OCTANOL: 60% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 24: (30% OCTANE:50%1-OCTANOL:20%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 25: (30% OCTANE:40%1-OCTANOL:30%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 26: (30% OCTANE:30% 1-OCTANOL:40% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 27: (30% OCTANE:20% 1-OCTANOL:50% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 28: (30% OCTANE: 10% OCTANOL: 60% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 29: (30% OCTANE: 0% OCTANOL: 70% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 30: (20% OCTANE: 60% 1-OCTANOL: 20% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 31: (20% OCTANE: 50% 1-OCTANOL: 30% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 32: (20% OCTANE:40% 1-OCTANOL:40% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 33: (20% OCTANE:30% 1-OCTANOL:50% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 34: (20% OCTANE : 20% 1-OCTANOL : 60% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 35: (20% OCTANE : 10% 1-OCTANOL : 70% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 36: (20% OCTANE:0%1-OCTANOL:80%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 37: (10% OCTANE:60%1-OCTANOL:30%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 38: (10% OCTANE: 50% OCTANOL: 40% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 39: (10% OCTANE: 40% OCTANOL: 50% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 40: (10% OCTANE: 30% 1-OCTANOL: 60% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 41: (10% OCTANE: 20% 1-OCTANOL: 70% 1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 42: (10% OCTANE:10% OCTANOL:80% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 43: (10% OCTANE:0% OCTANOL:90% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 44: (0% OCTANE:70%1-OCTANOL:30%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 45: (0% OCTANE:60%1-OCTANOL:40%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 46: (0%OCTANE:50%1-OCTANOL:50%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 47: (0%OCTANE:40%1-OCTANOL:60%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 48: (0%OCTANE:30%1-OCTANOL:70%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 49: (0%OCTANE:20%1-OCTANOL:80%1-OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.
APPENDIX 50: (0% OCTANE: 10% OCTANOL: 90% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.

APPENDIX 51: (0% OCTANE: 0% OCTANOL: 100% OCTYLAMINE). A) Rheology amplitude sweep, B) DSC melting temperature, C) Microscopy imaging.