PHASE BEHAVIOR OF 12-HYDROXYSTEARIC ACID GELS

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Thesis

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CHAPTER I

BACKGROUND

Introduction to Gels

Defining precisely what qualifies as a gel has been difficult due to the large number of definitions that have been employed over time.^{1,2} One of the earliest definitions states that materials that have permanent dimensions on the macroscale over an analytical time scale and have a continuous structure were defined to be gels.² Further, these materials have low moduli and solid-like rheological properties.

More recently, gels are taken to be materials that are composed mainly of a liquid solvent and a solid gelator that behave with solid viscoelastic properties. In such cases, a fluid solvent is held in place within a solid network of a gelator at low concentration. Capillary action and interfacial tension are the driving forces behind this immobilization.^{3,4}

The rheological definition of a gel states that a gel is a material with frequency independent storage and loss moduli, G' and G", respectively. Gels are elastic materials with G' greater than G".⁴

Because of the scope of these definitions, it has been necessary to separate gels into several subclasses; one method of doing so centers on the solvent that is immobilized. In the case where the solvent it water, these gels are referred to as hydrogels. Gels formed from other organic liquids are known as organogels. These subclasses are still quite broad.⁵

Another method of classifying types of gels depends on the method by which the solvent is immobilized. Gels can be formed by several mechanisms. These include chemical cross-linking, polymerization, physical entanglements, phase transitions and self-assembly.^{1,6,7}

Network formation can be the result of covalent bonding. These interactions lead to very stable gels that are chemically cross-linked.¹ In order to reverse these gels, enough energy must be applied to break the covalent bonds. Gels that can be thermally reversed generally contain self-assembled networks composed of noncovalent cross-links.⁶ Several types of polymers can self-assemble to form networks. These include semi-crystalline polymers which form networks as the crystalline domains on various chains aggregate and create cross-linking points.¹ Block copolymers are also suited to form networks; if the domains of the copolymer phase separate into multiple domains, these can be strong enough to form a stable network in solution.⁸

Small molecules are also capable of forming non-covalent networks in solution. One particular class of these materials of interest is networks formed from

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the crystallization of small molecules into long fibers that can further aggregate via hydrogen bonding.

Introduction to Low Molecular-Mass Organic Gelators

Low molecular-mass organic gelators (LMOGs) can be used to form gels in various solvent systems. There are a wide variety of small molecule compounds that can behave as gelators.⁹ LMOGs are composed of small molecules that are organic in nature that can self-assemble.⁶ This assembly is generally one-dimensional and results in the formation of long fibers. These fibers are then joined by bonding or physical entanglements to form a continuous network within a solvent. This diverse group of compounds allows LMOG driven gelation of a similarly wide array of solvents.^{9,10} This flexibility in components leads to a large number of possible applications.

Small molecules that have the capability to self-assemble in to fibers and thus be useful as LMOGs include structures based on sugars, many surfactant complexes, steroid-based molecules and peptide-based or pseudopeptide molecules.^{1,11,12} These types of molecules have the ability to assemble via non-covalent bonds.

Many gels are formed via non-covalent self-assembly.^{9,13} The resulting gels are less stable than those that are chemically cross-linked and can be reversed with an increase in temperature.⁹ Mechanisms for gel formation in these types of materials include crystalline fibers and worm-like micelle formation. Crystalline fibers can be formed via hydrogen bonding. Crystalline structures can also be formed via van der Waals forces as is the case when long-chain *n*-alkanes form gels.¹⁴

If the forces between the gelator molecules are too large or the interaction between the gelator and the solvent is highly unfavorable, macrophase separation can result leading to a crystalline precipitate rather than a network. This results in a system that cannot form a gel.¹⁵

The solid gelator forms a three dimensional network that traps the solvent in place via interfacial tension and capillary action.^{5,16} Small molecules also have the capacity to be used as gelators if they can interact with each other through hydrogen bonding or other non-covalent interactions.⁹ Gels formed in this manner will be thermally reversible. A schematic representation of the mechanism of gelation is shown below in Figure 1.



Figure 1: Schematic of gelation mechanism

Crystalline networks that form fibrillar structures as a result of intermolecular forces are an interesting class of materials that are able to gel solvents and can be used in many applications.

Applications

Gels consisting of LMOGs are of particular interest in many fields. These materials are suitable for many uses including as templates for porous materials and membranes, as biomaterials templates for scaffold formation, as thickening agents in cosmetics or food products, as drug delivery agents and as stimuli responsive materials.^{5,6,11,17–23}

Formation of reverse templates for the production of porous polymeric materials can be accomplished with LMOGs that are capable of gelling suitable monomers. Styrene can be gelled using 12-hydroxystearic acid. After polymerization, the remaining LMOG can be removed from the material via solvent extraction.



Figure 2: Porous styrene formed using an LMOG reverse template

The resulting voids will form an interconnected network of pores, as shown below in Figure 2. These materials may be useful in membranes or in mesoporous catayst applications.^{20–22}

Another potential application for materials containing LMOGs are for use as thickeners in cosmetics or food applications. In food applications, LMOGs can be used at low concentrations to solidify triacylglycerols and edible oils. These materials could be used in the manufacture of edible spreads as replacements for saturated or *trans* fats and to prevent oil separation and the breakdown of emulsions.¹⁸

Current Challenges

Current research in the field of LMOGs has not successfully been able to predict *a priori*, which compounds will gel a particular solvent.⁹ It is possible to empirically design new gelators.^{9,10} However, it is difficult to extend knowledge of systems that have been discovered to form gels to other systems due to the complex interplay of various factors affecting the gelation behavior of any particular solvent-gelator system.

Solubility parameters have been used to examine one of the factors controlling gelation ability in solvent-gelator systems.^{10,15,24,25} While certain empirical observations allow one to predict which solvents a particular gelator will gel, this method does not give a complete picture of the process of gelation.^{7,15}

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Another approach to designing gelators involves examining the thermodynamic behavior of the system. The behavior of these systems can be described using a phase diagram, as shown in Figure 3.



Figure 3: Representative phase diagram showing the liquidus and spinodal lines for a gelator-solvent system

Above the liquidus line, the system is composed of a homogenous solution of the gelator in the solvent. As the solution is cooled below the liquidus line, the gelator will begin to crystallize into long fibers that can then further aggregate to form a network.^{26–29} This network traps the solvent and prevents it from flowing, creating a semisolid gel. Below the spinodal line, the solution is unstable and will separate into two phases with any fluctuation in temperature.

Previous studies have shown that the sol-gel transition correlates to the melting temperature given by the liquidus line in the phase diagram.³⁰ Further

studies have shown that the degree of undercooling while forming a gel also impacts gel behavior.³¹⁻³⁵ Undercooling is the difference between the temperature to which the sol is quenched and the liquidus line at that concentration. Increasing the amount of undercooling increases the degree of supersaturation of the solution and thus the number of nuclei formed at the onset of crystallization.^{26,31} Changing the nature of the crystals formed during gelation will result in gels that have different fiber morphologies, optical properties and rheological properties.^{26,30,31}

There is currently an inability to design new gelators without experimentation.⁹ A method of predicting gelation ability through solubility parameters and a thermodynamic model would improve understanding of the entire process of gelation and allow LMOGs to be designed more easily. While there has been much interest in this field, relatively little work has considered the thermodynamic aspect of gelation in conjunction with the solubility parameter approach.⁹

CHAPTER II

THESIS OBJECTIVES

The driving hypothesis of this work is that the ability of a solvent-gelator system to form a gel should be related to the thermodynamic phase behavior of the system. Further, a relationship between the minimum gelation concentration and the thermodynamic phase behavior of the systems should be evident. There has been some effort in the field to interpret gelation behavior in terms of the thermodynamics, using solubility parameter theory and empirical expression for the melting point depression.^{10,15} This work will go a step further to measure the full phase diagrams of LMOG/solvent systems that are then fit with solution models that allow the gelation behavior to be directly connected to the thermodynamic behavior of the solutions.

Different solution models ranging from ideal, regular and Flory-diluent are used to fit the phase behavior of model LMOG solvent systems. In the ideal solution the only contributions to the free energy of mixing is the combinatorial entropy of mixing; the regular solution adds the excess enthalpy of mixing; and the Florydiluent model accounts for the disparity in size between the solvent and solute. To accomplish this 12-hydroxystearic acid, a model LMOG, is used for these investigations.

12-Hydroxystearic Acid

12-HSA is a saturated long chain fatty acid with one hydroxyl group on the aliphatic chain, as shown in Figure 4, and has been shown to be a good gelator. 12-HSA gels are used in many applications including as food and cosmetic thickening agents, organic electronic components and as aerogels.^{17,18,36} The wide range of potential applications as well as the use of related metal soaps in the lubrication industry has resulted in a large bank of information on 12-HSA being available. Additionally, the 12-HSA is readily available for testing purposes.





It has been shown that 12-HSA can aggregate into dimers, trimers, tetramers and other, higher order, aggregates.¹⁰ This is due to the interaction of the carboxylic acid groups via hydrogen bonding. The hydroxyl group is also capable of hydrogen bonding, further driving aggregation.

12-HSA is capable of forming gels that can be thermally reversed at low concentrations in organic solvents by crystalizing into a fibrous network driven by interaction hydrogen bonding. The fibers formed in solution are rigid and can be up to several micrometers long.³⁶ Crystallographic studies have shown that the width of the fibers is a multiple of the length of 12-HSA dimers formed by the hydrogen bonding of the carboxylic acid end groups. Elongation of the fibers is driven by hydrogen bonding at the hydroxyl group at position 12.^{10,36,37}

It has been shown that 12-HSA forms gels at compositions less than 3 wt% in a library of solvents containing long chain alkanes, cycloalkanes, long chain aldehydes, ethers, nitriles and thiols.¹⁰ Solvents with strong hydrogen bonding disrupt the crystal structure of 12-HSA resulting in solutions rather than gels. As a result, 12-HSA cannot gel alcohols, carboxylic acids or amines.¹⁰

The molecule is chiral which can influence the gelation behavior.^{37,38} The chiral center is located at position 12. It has been shown that racemic mixtures of 12-HSA are less able to form gels due to the growth of platelet structures rather than fibrils as is the case in optically pure D-12-HSA. In the case of gels formed in mineral oil, only 1 wt% D-12-HSA is necessary to form a gel, while more than 2 wt% is necessary in the case of racemic DL-12-HSA. The optically pure 12-HSA appears to organize along its transverse axis as dimers due to the carboxylic acid end groups hydrogen bonding. The racemic mixture is better able to form hydrogen bonds at the hydroxyl group at position 12 leading to in-plane growth of platelets.³⁷

12-HSA can be considered a model LMOG though it is unusual in several respects. 12-HSA has a low melting point relative to many other LMOGs and yet it can stabilize solvents in a gel form at very low concentrations. It also has a relatively low solubility parameter. Its utility as a LMOG is derived from the multiple hydrogen bonding sites that are available for intermolecular interactions. The end terminal carboxylic acid groups are highly available and will provide relatively strong hydrogen bonds allowing for the formation of 12-HSA dimers. The hydroxyl group at position 12 is also suitable for hydrogen bonding, though these interactions will be weaker than those of the carboxylic acid. These interactions are responsible for the growth of fibers and further aggregation in solution.

Solubility Parameters

Solubility parameters can be used to interpret the gelation behavior of systems containing LMOGs. Solubility parameters give a way to quantify the level of interaction between two or more components and thus the solubility of the components. Materials with similar solubility parameters will be miscible.

Several theoretical group contribution methods have been developed that allow for the calculation of solubility parameters based on the structure of the molecules in question as they are often difficult to find experimentally. Hildebrand solubility parameters (δ) have been used for a long time and the theory has been further refined by Hansen (δ_t). This newer theory divides molecular interactions into three components: polar (δ_p), hydrogen bonding (δ_h) and dispersive (δ_d) interactions.

The solubility parameter approach to LMOG design has been studied in various systems. Solubility parameter studies have been carried out on LMOGs derived from steroids, sugars, and amides, as well as on 12-HSA.^{10,13,30,39,40}

The hydrogen bonding Hansen solubility parameter has been used to predict the ability of 12-HSA systems to from gels.¹⁰ A large number of solvents were tested for gel formation including apolar, polar and hydrogen bonding solvents that covered the range of dispersive Hansen parameters from 14 to 20 MPa^{0.5}. All samples were prepared with 12-HSA concentrations of less than 3 wt%. The gelation behavior was compared to the Hansen solubility parameter and each of the contributions. The results of the study show that only the hydrogen bonding Hansen solubility parameter are useful for the prediction of the ability of 12-HSA to form a gel in a particular solvent.¹⁰ Specifically, it was found that a solvent δ_h less than 4.7 MPa^{0.5} resulted in clear gels, solvent δ_h values between 4..7 and 5.1 MPa^{0.5} resulted in opaque gels and solvent δ_h values greater than 5.1 MPa^{0.5} resulted in formation of solutions rather than gels.¹⁰ The data in this study are based upon the ability of 12-HSA to form a gel at concentrations below 3 wt%.

This correlation between of the gelation behavior and the solubility parameters of LMOG solutions imply that the solution phase behavior has an important influence on the gelation behavior. ^{10,24,41} Therefore, a logical step is to directly characterize the solution phase behavior of model LMOG-solvent systems to determine its role on the gelation behavior. ^{30,38}

Regular Solution and Flory-Huggins Theory

LMOG systems have been shown to exhibit non-ideal solution behavior.¹⁵ This is potentially due to both the interactions between the solvent and LMOG giving rise to non-ideal enthalpies of mixing and the different sizes of the solvent and LMOG molecules giving rise to non-ideal entropies of mixing. These two effects increase the complexity of fitting experimental data.

One method of modeling non-ideal solution behavior is the regular solution model.^{25,42} Regular solutions are assumed to have a non-zero enthalpy of mixing due to interactions between the solute and the solvent. Like ideal solutions, the components have equal molar volumes, zero volume change upon mixing and the solution is well-mixed. In regular solution theory, an additional interaction parameter, χ , is used to quantify the excess enthalpy of mixing of the system.

In the case of a regular solution, the Gibbs free energy of mixing, ΔG_m , is given by

$$\frac{\Delta G_m}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + x_1 x_2 \chi \tag{1}$$

where x_1 and x_2 are the mass fractions of component 1 and 2, respectively.

The interaction parameter can be estimated using solubility parameters for components 1 and 2, δ_1 and δ_2 , respectively, as follows

$$\chi_{12} \approx \frac{V}{RT} (\delta_1 - \delta_2)^2 \tag{2}$$

The temperature dependence of χ can most simply be given by

$$\chi_{12} = \frac{A}{T} \tag{3}$$

However, for the purpose of fitting experimental data, it is useful to represent χ in terms of two parameters, *A* and *B*

$$\chi_{12} = \frac{A}{T} + B \tag{4}$$

where

$$A = \frac{V}{R} (\delta_1 - \delta_2)^2 \tag{5}$$

and the parameter *B* is empirical in nature.

The addition of the parameter *B* can result in better fits when Equation 3 does not exactly represent the temperature dependence of χ . Further empirical parameters can be used to improve the quality of the fit; however the increase in the number of parameters may result in fits which are difficult to explain theoretically and contain parameters with no real physical meaning.

The Flory-Huggins theory, as given in Equation 4, provides a relationship between melting temperature of the pure crystalline component, i.e. 12-HSA, and the volume fraction of the components. The change to volume fraction from mass fraction in the Flory-Huggins equation allows for the addition of degrees of polymerization of one or both components. This allows for the fitting and prediction of liquidus lines for a particular system with components having different molar volumes. The means to adjust the degree of polymerization of each component allows one to better describe the behavior of the system. Flory-Huggins theory can be used to predict the melting temperature of the gelator as a function of composition as follows

$$T_{m,2} = \frac{\frac{\Delta H_{f,2}^0 V_S}{V_2 R} + A\phi_1^2}{\frac{\Delta H_{f,2}^0 V_S}{V_2 R T_{m,2}^0} - \frac{1}{N_2} \ln \phi_2 - (\frac{1}{N_2} - \frac{1}{N_1})\phi_1 - B\phi_1^2}$$
(6)

where $\Delta H_{f,2}^0$ is the enthalpy of formation of the gelator, V_s is the molar volume of the solvent, V_2 is the molar volume of the gelator, R is the universal gas constant, ϕ is the 15

volume fraction, and $T_{m,2}^0$ is the melting point of pure gelator. N_1 is the degree of polymerization of the solvent and is taken to be one in all cases.

The enthalpic contribution to the interaction parameter is described by *A* while *B* is attributed the entropic contribution of the system.

High Boiling Point Solvents

The thermodynamic behavior of LMOG-based gels was examined in solutions of organic solvents with high boiling points. This allowed for the collection of melting points using DSC rather than relying upon temperatures of gelation.

This is beneficial as the gel transition temperature may vary significantly depending upon the definition used to define gel behavior and is a highly subjective method. By choosing solvents with high boiling points, it is possible to use DSC to measure the melting points of these gels resulting in repeatable liquidus lines. It is also possible to reach the high gelator concentrations necessary to complete a phase diagram of these materials that cannot be reached in systems containing solvents with low boiling points.

Phthalates are used commercially as plasticizing agents and are esters of phthalic acid.⁴³ The general structure of a phthalate is shown in Figure 5. Phthalates have the ability to participate in hydrogen bonding and can thus interact with 12-HSA leading to complex gelation behavior. In this study, symmetric phthalates were used.



Figure 5: Chemical structure of a generic phthalate

This group of solvents was chosen to be the main focus of the study due to their high boiling points. DMP, the smallest of the selected solvents, boils at 282°C, well above the necessary temperature necessary for melting point characterization.

A series of phthalates and phenolic solvents were selected for use in this study. The choice of phthalates results in a large library of similar compounds that can easily be studied due to their wide availability.⁴³ Alkyl chains of varying lengths were selected to spread the solvents into as wide a solubility parameter space as possible. The Hansen solubility parameter of dimethyl phthalate (DMP) is 22.1 MPa^{0.5} while that of ditridecyl phthalate (DTDP) is 17.6 MPa^{0.5}. This creates a range of solubility parameters that starts below and ends above that of 12-HSA.

The phenolic solvents were chosen as they do not interact with the gelator through hydrogen bonding as is the case with the phthalates. Long chain alkanes were also selected to further decrease the solubility parameter of the solvents to examine the thermodynamic behavior when the solvent quality decreases.

The gelation behavior of a particular gelator-solvent system is dependent on many thermodynamic properties including the level of undercooling during the formation of the gel. This makes it important to know the thermodynamic properties of the system in question.

CHAPTER III

EXPERIMENTAL METHODS

Purification of 12-HSA

12-HSA was purchased in technical grade and was further purified using recrystallization. Recrystallization was performed twice. Acetone was the purification solvent which was removed by drying overnight *in vacuo*.

Gel Preparation

Gels were formed by mixing 12-HSA and the solvent and heating the mixture to 90°C until a transparent, homogenous solution was formed. Dissolution required a minimum of 30 minutes. The solution was then quenched to 25°C for twenty minutes. Solutions that were suspended and did not flow when the vials were inverted were determined to be gelled.

Samples were prepared with concentrations of 1, 2 and 5 mol% 12-HSA and 10 to 90 mol%, inclusive, in 10% increments in dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), dioctyl phthalate (DOP), diisodecyl phthalate (DIDP) and ditridecyl phthalate (DTDP). Non-phthalate solvents diethyl malonate (DEM), 1-methyl naphthalene (1MN), phenol cyclohexane (PCH), diphenyl

methane (DPM) and dodecane (C12) were similarly prepared. Solvents were used as received.

Differential Scanning Calorimetry

The melting temperature (T_m) of each gel was determined using differential scanning calorimetry (TA Instruments Q2000). Samples were prepared by placing a small amount of gel into an aluminum pan which was then sealed. Two heating cycles were performed. Samples with molar concentrations greater than 10% were heated from 25°C to 130°C at a rate of 10°C per minute. Between heating cycles samples were isothermal at 130°C for 3 minutes to ensure complete melting and then quenched to 25°C over 4 minutes and were isothermal for 7.5 minutes before the second cycle. Samples with lower concentrations were heated from -10°C to 130°C and were isothermal for 15 minutes at -10°C between heating cycles; the remainder of the procedure was unchanged.

Gel Transition Temperature

The gel transition temperature (T_{gel}) was determined by heating gelled samples in 1°C increments in a thermostated aluminum block until flow was detected when the vial was inverted. The first temperature at which flow was exhibited was determined to be the gel transition temperature. Samples were allowed to equilibrate at each temperature for 10 minutes.

Minimum Gelation Concentration

The minimum gelation concentration at 25°C, 40°C and 60°C was determined by diluting gels by 0.05 mL (25°C) or 0.25 mL (40°C and 60°C) and reheating to 90°C and quenching to the specified temperature in a temperature controlled aluminum block. Samples that still exhibited flow after twenty minutes were determined to be below the minimum gelation concentration.

Calculation of Solubility Parameters

Solubility parameters for 12-HSA and each solvent for which literature values were unavailable were calculated using group contribution methods. The Hildebrand solubility parameter and molar volume was calculated following Fedors method.⁴⁴ Fedors method is a group contribution method and values for the cohesive energy at 298K, $E_{coh}(298)$ and molar volume, V, have been tabulated for each functional group. The Hildebrand solubility parameter, δ , is calculated using Equation 3.

$$\delta = \sqrt{\frac{E_{coh}(298)}{V}} \tag{3}$$

The Hoftyzer and van Krevelen method was used to calculate the Hansen solubility parameter and the individual contributions to the Hansen solubility parameter for those solvents where literature values were unavailable.⁴⁴ Equations 4, 5 and 6 give the dispersion, polar and hydrogen bonding components of the Hansen solubility parameter, δ_d , δ_p and δ_h , respectively. Equation 7 gives the total

Hansen solubility parameter, δ_t . F_{di} , F_{pi} and E_{hi} are the group contributions of dispersive, polar and hydrogen bonding interactions, respectively.

$$\delta_d = \frac{\sum F_{di}}{V} \tag{4}$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \tag{5}$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}} \tag{6}$$

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \tag{7}$$

Data Fitting

The melting points of the gel samples for a particular solvent were fit to the Flory-Huggins model by minimizing the sum of the squares of the residuals. The interaction parameter, *A*, was calculated using Hansen solubility parameter values taken from the literature^{10,45} or calculated from group contribution theory as shown in Equations 4-7. The enthalpy of formation of the pure 12-HSA, $\Delta H_{f,2}^0$, was allowed to vary, as was the degree of polymerization of the 12-HSA, N_2 and the fit parameter, *B*.

CHAPTER IV

PHASE BEHAVIOR OF 12-HYDROXYSTEARIC ACID GELS

Systems of 12-HSA in high boiling point solvents have been investigated to determine the relationships between the thermodynamic phase behavior and the gelation behavior. The solvents of interest were largely composed of a library of dialkyl phthalates.

Phthalates were used due to their ready availability with a large number of alkyl chain lengths and the variation in the solubility parameter with the change in the length of the alkyl chains. A range of solubility parameters used allowed for the ability to determine gel behavior in a wide cross-section of possible gelator-solvent systems.

Other high boiling point solvents including dodecane, diethyl malonate and three additional phenolic solvents were also used to increase the range of Hansen solubility parameter contributions examined. The molar volumes and solubility parameters for the systems used are shown in Table 1.

		Solubility Parameter (MPa ^{0.5})				
		Hildebrand ⁺	Hansen			
	V (mL/mol)†	δ	δ_{d}	δ_{p}	$\delta_{\rm h}$	δ_t
DMP	163.0	22.3	18.6	10.8	4.9	22.1
DEP	198.0	21.6	17.6	9.6	4.5	20.5
DBP	266.0	20.6	17.8	8.6	4.1	20.2
DOP	377.0	19.4	16.6	7.0	3.1	18.3
DIDP	464.2	19.1	16.6	6.2	2.6	17.9
DTDP	558.3	19.0	16.6	5.4	1.9	17.6
DCP*	263.4	21.8	20.1	2.7	7.2	21.5
1MN	138.8	21.0	20.6	0.8	4.7	21.1
C12	228.6	16.1	16.0	0	0	16.0
DEM*	119.1	20.6	16.1	7.7	8.3	19.7
DPM*	158.9	20.8	19.7	1.4	0	19.7
PCH*	170.7	19.1	17.3	0.7	0	17.3
12-HSA*	312.5	21.1	16.6	2.86	6.8	18.1

Table 1: Solvent and gelator solubility parameters^{10,45}

*Hansen values calculated by group contribution⁴⁴

⁺Hildebrand values and molar volumes calculated by group contribution⁴⁴

The gelation temperature of these systems was examined. Gels were slowly heated until they began to exhibit flow when inverted. This point was determined to be the gel transition temperature. The gel transition temperature was then compared to the thermodynamic melting temperature as determined by DSC measurement.

The minimum gelation concentration of samples prepared from these solvent-gelator systems were examined using sequential dilutions. A small amount of solvent was added at each dilution and the minimum gelation concentration was determined to be the concentration at which any further dilution would result in gels that exhibited any amount of flow when inverted, i.e. the gel transition temperature was the same as the temperature of interest.

Gel-Sol Transition

The choice of high boiling point solvents for this study resulted in the completion of phase diagrams for all solvents over the entire range of composition, as shown in Figure 6. In systems involving solvents with low boiling points, it is not possible to use DSC to attain a melting temperature when the gels are stable at higher temperatures than the boiling point of the solvent. In these cases, it is necessary to rely on other methods of interrogating the thermal behavior of the gel; these methods include determining the gel transition temperature or the cloud point of the system.



Figure 6: Phase diagram of 12-HSA in DOP showing T_m and T_{gel}

In the systems examined, the gel transition temperature is generally several degrees lower than the melting temperature of the gels as determined by DSC. The gelation temperature is recorded as the temperature at which the gel first begins to flow and the melting temperature is defined as the peak temperature during melting from the DSC trace. The gelation temperature is more similar to the temperature recorded at the start of the DSC peak. At this point, enough of the crystalline network has melted due to the distribution of melting temperatures of the crystals and the network junctions for some of the trapped liquid to begin to flow. Only a small fraction of the gelator network point must dissociate to create liquid regions in the gel which can flow under the force of gravity.

Another method of examining the transition from the gel to sol is the cloud point temperature which is defined as the temperature at which the solid particles are all completely dissolved into solution and the sample becomes optically clear. This temperature is closer to the melting temperature than the gelation temperature but is consistently a few degrees higher than the melting temperature. In the case of the cloud point, the crystalline network must be dissolved completely for the solution to become optically clear. Any remaining crystalline particles larger than the wavelength of light will cause noticeable scattering resulting in solutions that are not optically clear.

DSC traces for 12-HSA in DBP are shown below in Figure 7. The position of the peak shifts to higher temperature as the concentration of 12-HSA is increased.



Figure 7: DSC traces for 12-HSA in DBP over the range of compositions from 1 mol% (top trace) to 90 mol% (bottom trace). Exothermic heat flow up.

The melting peaks become broader and shallower at low concentrations of 12-HSA as shown in the top curves in Figure 7. The formation of gels at these low concentrations seems to be highly dependent on the kinetic behavior of the system and it can be difficult to obtain gels that can reliably be made to exhibit the same properties as previous gels of the same composition.

The enthalpy of melting of each gel can be determined by integrating the area of each peak. The enthalpy measured by DSC is widely scattered when compared with the expected value at a given concentration of 12-HSA in each sample, as shown in Figure 8. The enthalpy was determined from the DSC traces of each concentration of 12-HSA in the solvents measured.



Figure 8: Enthalpy of formation of 12-HSA calculated from DSC peak area for the phthalate series

The data above were averaged for each of the solvents and then was compared with the Hansen solubility parameter of the solvent. As shown below in Figure 9, the measured enthalpy of melting increases with the hydrogen bonding Hansen solubility parameter.



Figure 9: Enthalpy calculated from DSC peak area increases with the hydrogen bonding Hansen solubility parameter

Minimum Gelation Concentration

12-HSA proves to be a good gelator for the solvents of interest because of the very low concentrations necessary to form a gel, as shown in Table 2. 12-HSA is well suited to gel solvents due to the strong hydrogen bonds that form with other 12-HSA molecules.

-	MGC (mol ₁₂ -HSA/mol _{Solvent})			
	<u>25°C</u>	<u>40°C</u>	<u>60°C</u>	
DMP	0.0075	0.0374	0.2505	
DEP	0.0078	0.1002	0.2498	
DBP	0.0108	0.0999	0.2495	
DEHP	0.0097	0.1014	0.2501	
DIDP	0.0108	0.0204	0.2496	
DTDP	0.0158	0.0093	0.2512	
DCP	0.0079	0.0165	0.2009	
1MN	0.0050	0.1463	0.5747	
DEM	0.0035	0.0298	0.2581	
DPM	0.0046	0.1549	0.6356	
РСН	0.0040	0.1639	0.4962	

Table 2: Minimum gelation concentration

For the three temperatures examined, the amount of 12-HSA necessary to form a gel increases as the Hansen hydrogen bonding parameter increases.



Figure 10: Minimum gelation concentration versus the total Hansen solubility parameter.



Figure 11: Minimum gelation concentration versus the dispersive component of the Hansen solubility parameter.



Figure 12: Minimum gelation concentration versus the polar component of the Hansen solubility parameter.



Figure 13: Minimum gelation concentration versus the hydrogen bonding component of the Hansen solubility parameter.

The increase in minimum gelation concentration with temperature is likely due to the fact that there are increased interactions between 12-HSA and the solvent as the amount of hydrogen bonding between them increases. The formation of a gel is dependent on enough 12-HSA molecules interacting with each other to selfassemble into a crystalline network to trap the solvent via capillary action. This critical concentration will be higher if 12-HSA molecules are distributing their hydrogen bonding between inter- and intra-species interactions.

To form gels at higher temperatures, a higher concentration of gelator was required and this amount was similar for all the solvents tested here, regardless of solubility parameter. Samples of high concentration have similar sol-gel transistion temperatures across the solvents used due to the approach of all the liquidus lines to the melting point of pure 12-HSA.

The amount of undercooling necessary to form a gel at the minimum gelation concentration was also measured at three temperatures, as shown in

Table 3. Undercooling is the drop in temperature below the liquidus line measured by DSC necessary to form a gel at a given concentration. The formation of a gel generally required some amount of undercooling in the systems studied. The degree of undercooling necessary is dependent on the solvent selected and the temperature at which the gel is to be formed. For gels with lower gelator concentrations, the amount of undercooling necessary was increased.

	Undercooling (°C)			
-	<u>25°C</u>	<u>40°C</u>	<u>60°C</u>	
DMP	15	17	3	
DEP	25	21	5	
DBP	19	13	0	
DEHP	19	19	5	
DIDP	23	10	4	
DTDP 22		7	4	
DCP	39	24	1	
1MN	13	9	2	
DEM		6	3	
DPM		19	5	
РСН	19 17 3		3	

Table 3: Undercooling necessary to form a gel at the MGC

Each solvent shows an increase in the degree of undercooling necessary to form a gel as the concentration of 12-HSA decreases. The amount of undercooling

necessary does not seem to depend strongly on the solubility parameters of the system, however.

Fit Results

Fitting the temperature of gelation versus concentration data can be achieved using several different models. In order of increasing complexity these are the ideal solution, regular solution and Flory-Huggins models. Adding parameters will necessarily improve the ability of a particular model to fit a collection of data, however, a case must be made as to the physical nature of any constants used in order to have a meaningful fit.

The ideal solution model is comprised of the simplifying assumption that the interactions between solute and solvent molecules are indistinguishable from the interaction between both solute-solute and solvent-solvent interactions, i.e. there are no specific interactions of any type. As a result of this assumption, the enthalpy of mixing must be equal to zero, the volume of the mixture is simply the addition of the volumes of the two components of the solution and the fact ideal solutions must always be completely miscible.

In the case of 12-HSA in the high boiling point solvents of interest here, the ideal solution model would not be expected to produce realistic results; the molecules making up the solute and solvents are dissimilar and there will be differences in their interactions. The ability of these solute-solvent pairs to interact

via specific interactions such as hydrogen bonding will lead to significant deviation from ideal solution behavior, as shown below in Figure 14.



Figure 14: Ideal solution fit of the liquidus line of 12-HSA in DOP

One method of accounting for the non-idealities of more complex solutions such as those of interest here is the use of the regular solution model. The regular solution model removes the assumption that there is no enthalpy of mixing that was made in the ideal solution model. The regular solution model assumes that the non-ideal solution behavior is due to only the interactions between the solute and the solvent. Further, it is assumed that these interactions can be described using an interaction parameter, χ .

As shown in Figure 15, the regular solution model over predicts the melting point of 12-HSA in the more concentrated sample while under predicting the melting point at low concentration.



Figure 15: Regular solution fit of the liquidus line of 12-HSA in DOP

As LMOGs such as 12-HSA are proposed to be used at low concentrations to gel solvents, it is important to increase the accuracy of the prediction at concentrations less than 1%. A model that under predicts the melting point of the system will result in a higher apparent minimum gelation concentration and, as such, a potential gelator could be ignored due to the artificially high concentration necessary to gel a particular solvent. In Figure 16, the phase diagrams of the solvents tested show considerable overlap regardless of their differing solubility parameters. These systems are more complex than can be modelled exclusively using the change in solubility parameters. There are other influences that determine the phase diagrams of these components. One such factor is likely the change in the aggregation of the solute molecules. This is a result of the presence of interactions not only between solute and solvent molecules but also between solute molecules. It is also the case that the solvent molecules can interact with one another.



Figure 16: Overlaid phase diagrams of the solvents tested as determined by DSC

12-HSA is capable of forming dimers, tetramers and higher order aggregates in solution. This behavior was fit to the Flory-Huggins equation by treating 12-HSA as a monomer unit and using the degree of polymerization to capture the average number of monomers per aggregate, D_{agg} .

$$D_{agg} = \frac{N_2 V_S}{V_2} \tag{3}$$

The conversion to D_{agg} from the degree of polymerization of 12-HSA, N_2 , is necessary as the fit parameters are calculated using the molar volume of the solvent as the basis for the Flory-Huggins site volume. The resulting fits are quite good and rely only on two parameters and one additional fitting constant. Results of the fitting are shown in Table 4.

	N2	Dagg	В	∆ <i>H_f0</i> (^J /g)
DMP	2.60	1.36	0.40	126.6
DEP	2.85	1.81	0.67	127.8
DBP	3.90	3.32	0.20	125.0
DOP	3.01	3.63	0.73	106.0
DIDP	3.96	5.88	0.62	89.69
DTDP	2.30	4.11	0.75	94.02
1MN	16.7	7.42	0	136.4
C12	6.67	4.88	0.52	125.5
DEM	4.72	1.80	0.62	203.0
DPM	2.20	1.12	1.1	117.0
РСН	17.5	9.56	0.16	169.7

Table 4: Flory-Huggins fitting results

Figure 17 shows the phase diagram of 12-HSA in DOP and the Flory-Huggins fit to the liquidus line.



Figure 17: Flory-Huggins fit of the liquidus line for a binary system of 12-HSA in DOP

Treating the 12-HSA simply as a component that cannot aggregate, as in the regular solution model, yields fits of poor quality. The melting and gelation behavior is controlled by both entropic and enthalpic effects. When the 12-HSA aggregates, it behaves as if it were a much larger molecule resulting in a significant change in the entropic interactions between the gelator and the solvent. This leads to increased complexity in system behavior due to the variable nature of 12-HSA aggregation. A more representative schematic of gelation in systems containing 12-HSA is presented on the following page in Figure 18.



Figure 18: Schematic of gelation showing aggregated gelator

The Flory-Huggins model can be used to capture the added complexity of the interactions between solute molecules. As shown in Figure 17, the fit is significantly improved over the simplified fits that result from use of the regular solution model.



Figure 19: Average number of aggregates, fit parameter B and the difference in total Hansen solubility parameters in relation to the hydrogen bonding component of the Hansen solubility parameter

The resulting Flory-Huggins fit parameters show a convincing trend when the degree of aggregation, D_{agg} , of 12-HSA is plotted against the hydrogen bonding component of the Hansen solubility parameter, as shown in Figure 19 on the previous page.

As the Hansen hydrogen bonding parameter increases, the degree of aggregation generally decreases. The fit constant, *B*, is generally within the range (0.2 to 0.6) that has been previously observed.⁴² A higher Hansen hydrogen bonding parameter indicates that there are increased hydrogen bonding interactions between the solute and the solvent. It can be surmised that the increasing interactions with the solvent decrease the relative energy penalty that occurs when the 12-HSA remains in solution as a single molecule rather than an aggregate of two or more molecules.

With regard to the minimum gelation concentration and the degree of undercooling necessary to form a gel, there is little evidence of a trend with respect to the Hansen hydrogen bonding parameter.

The values of the enthalpy of formation of pure 12-HSA, $\Delta H_{f,2}^0$, are also very similar to those calculated from the DSC trace when they are treated as variables in the Flory-Huggins fit, as shown on the following page in Figure 20.



Figure 20: Enthalpy of melting values calculated from DSC traces and Flory-Huggins fit values of enthalpy of formation of pure 12-HSA

It is possible to fit these systems by setting $\Delta H_{f,2}^0$ as a constant. The fit parameter, *B*, is changed as a result. Increasing the value of *B* seems to modify the fit curve in qualitatively the same way that increasing the value of $\Delta H_{f,2}^0$ does. It seems that the fit parameter *B* can be said to describe the entropic contribution to the behavior of the system. The entropic and enthalpic contributions are both determined by the exact nature of the components of the system and can balance each other; if the enthalpic contribution to the fit is decreased by setting $\Delta H_{f,2}^0$ to a value that is predicted by the Flory-Huggins model, the fit parameter *B* will be increased to compensate for this and a different balance between enthalpic and entropic driving forces will emerge. Control fits were also performed. The degree of polymerization of the solvent, N_1 , was also allowed to vary and was found to improve the fit only slightly when set to approximately 0.9. It is encouraging that this value is close to 1 which is the expected value if the solvent molecules do not interact with one another.

There is little evidence of a change in gelation behavior over the range of solvents. This is likely due to the competing effects of the change in the Hansen hydrogen bonding parameter of the solvent and the change in the total Hansen solubility, as shown above in Figure 19.

The average number of molecules per 12-HSA aggregate decreases as the Hansen hydrogen bonding parameter increases. This is likely due to the interaction of the 12-HSA with the solvent. In the case of solvents that can hydrogen bond, there are interspecies interactions that interrupt 12-HSA aggregates. In those solvents that are unable to hydrogen bond, i.e. solvents with a Hansen hydrogen bonding parameter of zero, the aggregates are largest as there are no 12-HSA solvent hydrogen bonding interactions in the system. In the case of our library of solvents, the change in the Hansen hydrogen bonding parameter is balanced by the drop in solvent quality, driven by the change in the total Hansen solubility parameter as shown in Figure 19.

In order to find trends in future data sets, solvents should be selected not only on the basis of their total solubility parameter; the Hansen hydrogen bonding component of the solubility parameter should also be taken into account. This will ensure that the effect of the competing solution behaviors will not be masked by one another.

The fit parameter *B* may be responsible for capturing the distribution of aggregate size over the range of compositions. At high concentration, there is a higher driving force for 12-HSA to form aggregates. At low concentrations, where the driving force for aggregate formation is lower, the number of molecules present per aggregate should also decrease.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The Hansen solubility parameters studied here have been shown to have some effect on the ability of 12-HSA solutions to gel. The Hansen hydrogen bonding parameter in particular has a large effect on the minimum gelation concentration of these systems.

It can be concluded that the method of fitting DSC melting points of gels formed by LMOGs in organic solutions can be fit experimentally using the Flory-Huggins theory. The fits obtained have been shown to yield physically reasonable parameters even when control fits are allowed to vary parameters of the system generally reserved as constants.

Recommendations

In future studies, all components of the Hansen solubility parameters should be examined to find a wide range of solvents that will provide as much variation in gel behavior as possible. The 12-HSA should be verified to be optically pure and not racemic. Racemic mixtures will result in a lower pure substance melting point in the Flory-Huggins equation.

The presence of polymorphs should be studied using WAXS. If polymorphs are present in the solute-solvent pairs studied, this must be taken into account when the data are fit using Flory-Huggins theory. The melting point to the pure substance will decrease if polymorphs are present.

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APPENDIX

This appendix contains DSC traces for each of the 12-HSA solvent systems studied. The DSC traces are presented with exothermic heat flow up. The phase diagram for each 12-HSA solvent system is also included. These plots show the melting temperature, T_m , as determined from the presented DSC traces and the gel transition temperature, T_{gel} , as determined by the heat and tilt method. The Flory-Huggins fit line is included labeled T_m Fit.

Dimethyl Phthalate





Diethyl Phthalate





Dibutyl Phthalate





Dioctyl Phthalate





Diisodecyl Phthalate





Ditridecytl Phthalate





1-Methylnapthalene





Diethyl Malonate





Diphenylmethane





Phenolcyclohexane





Dodecane



Dicyclohexyl Phthalate

