Mixed Saturated−Unsaturated Alkyl-Chain Assemblies: Solid Solutions of Zinc Stearate and Zinc Oleate

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The linear saturated stearic acid and the bent mono-unsaturated oleic acid do not mix and form solid solutions. However, the zinc salts of these acids can. From X-ray diffraction and DSC measurements we show that the layered zinc stearate and zinc oleate salts form a homogeneous solid solution at all composition ratios. The solid solutions exhibit a single melting endotherm, with the melting temperature varying linearly with composition but with the enthalpy change showing a minimum. By monitoring features in the infrared spectra that are characteristic of the global conformation of the hydrocarbon chain, and hence can distinguish between stearate and oleate chains, it is shown that solid solution formation is realized by the introduction of gauche defects in a fraction of the stearate chains that are then no longer linear. This fraction increases with oleate concentration. It has also been possible from the spectroscopic measurements to establish a quantitative relation between molecular conformational order and the thermodynamic enthalpy of melting of the solid solutions.

Introduction

Linear and bent rodlike molecules do not mix. The linear saturated fatty acid, stearic acid, and the bent mono-unsaturated fatty acid, oleic acid (*cis*-9-octadecanoic acid), for example, do not form a solid solution at any composition ratio.[1] This is understandable; it is difficult to pack the linear stearic acid with the bent oleic acid. Even elaidic acid (*trans*-9-octadecanoic) in which the segments on the either side of the double bond are trans and hence the molecule "nearly" linear does not form a solid solution with stearic acid except over an extremely narrow composition range.[1] These molecules also do not mix in Langmuir−Blodgett films. Stearic and elaidic acids, for example, are immiscible in monolayers irrespective of the surface pressure.[2] There are, however, natural situations like lipid "rafts" in cell plasma membranes in which submicron domains of sphingolipids that contain mostly long-chain saturated acyl chains coexist with glycerophospholipids that consist of unsaturated acyl chains that have a "kinked" or bent structure.[3−5] The sphingolipids pack effectively and hence their melting temperatures are higher than those of the corresponding bent glycerophospholipids. It has been suggested that it is the differential packing ability that leads to differential miscibility and hence to phase segregation in the membrane.[6] A variety of biological functions have been attributed to these structures.[3,4]

Here we report that zinc salts of the saturated stearic acid and the unsaturated oleic acid can form homogeneous solid solutions over the entire composition range. These compounds were chosen for this study because zinc stearate (ZnSt), unlike most other polyvalent metal soaps, is known to pass directly from the solid to liquid phase at 403 K,[7] without the complication of any intermediate mesophases.[8,9] In zinc oleate (ZnOl), on the other hand, the presence of the double bond in the middle of the chain effectively decouples the thermal evolution of conformational disorder in the chain segments on either side of the double bond, and the melting of each of these segments in the assembly occurs as an independent event.[10] Although crystal structures of ZnSt and ZnOl have not been reported, on the basis of X-ray absorption,[11] diffraction,[7,8,12] and infrared spectroscopic studies,[7,10,12] it has been established that these compounds have a layer structure with tetrahedrally co-coordinated Zn cations connected by carboxylate bridges to four stearate/oleate chains. We had shown previously that in ZnSt the alkyl chains of the bilayer adopt an all-trans conformation with all 16 methylene units of the stearate chain in trans registry while in ZnOl the 7 methylene units on either side of the double bond are organized in all-trans segments.[7,10] On melting, the coordination of the carboxylate to zinc changes from bridging bidenate to one that has considerable monodentate character, resulting in the breakup of the inorganic sheets.[7] Metal coordination plays an important role in the thermal stability of these compounds. Both ZnSt and ZnOl are solids at room temperature, each with a melting point considerably higher than that of the corresponding fatty acid.[10] Coordination also defines the closest interchain distance in the soap, 4.69 Å, which is the Zn−Zn distance in the layer.[11] In the corresponding fatty acids the interchain distance is considerably smaller, typically 3.7 Å.[13] Here we have used DSC and X-ray diffraction measurements to establish that ZnSt and ZnOl form a solid solution over the entire composition range and vibrational spectroscopy to understand how small changes in conformation allow stearate and oleate chains to pack together to form $ZnSt_xOl_{(1-x)}$ solid solutions.

Experimental

ZnSt and ZnOl were prepared by addition of aqueous solutions of the sodium salt of the corresponding fatty acid to $ZnCl_2$ solution. The resulting precipitate was washed with ethanol and water. Solid solutions of ZnSt and ZnOl, ($ZnSt_xOl_{(1-x)}$) were prepared by mixing the required quantities of ZnSt and

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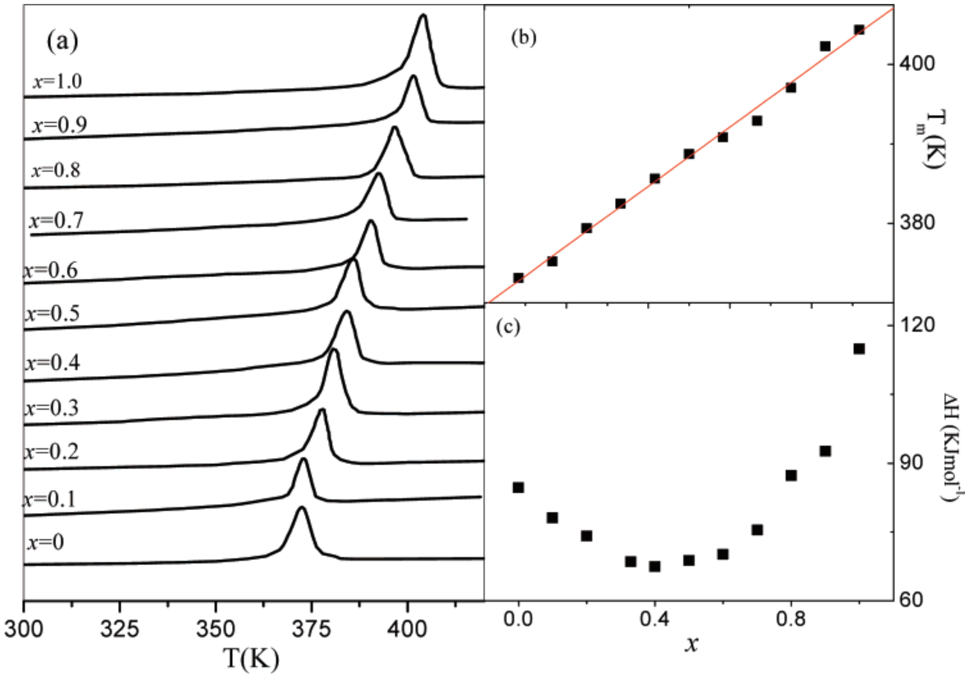

Figure 1. (a) DSC traces of $ZnSt_xOl_{(1-x)}$ for different compositions. Variation of (b) the melt transition temperature, T_m, and (c) enthalpy change, ΔH, with composition.

ZnOl, heating to above the melt temperature (410 K), and then cooling to ambient temperature.

Differential scanning calorimetric (DSC) measurements were recorded on a Perkin−Elmer DSC-2C instrument operated at a scanning rate of 5 K/min under N_2 atmosphere. The temperature scale and enthalpies were calibrated using an indium standard. Powder X-ray diffraction patterns were recorded on a Shimadzu XD-D1 diffractometer using Cu Kα radiation. Variable-temperature infrared spectra were recorded on a Perkin−Elmer spectrum 2000 FT-IR spectrometer in the diffuse reflectance mode using a DRIFT (P/N 19900 series) accessory with a cooled MCT detector.

Results and Discussions

Thermal Studies. The DSC traces for different compositions of $ZnSt_xOl_{(1-x)}$ are shown in Figure 1a. All compositions show a single reversible endotherm with the melting transition temperature lying between that of the end members, ZnSt (403 K) and ZnOl (373 K).[14] The melt transition temperature shows a linear variation with composition (Figure 1b). The enthalpy change associated with the endothermic melting transitions is, however, not linear and has a minimum at a composition with $x = 0.4$ (see also Supporting Information). This behavior of $ZnSt_xOl_{(1-x)}$ may be contrasted with that of the corresponding mixtures of fatty acids, stearic and oleic acids, that do not form solid solutions and whose DSC shows two transitions corresponding to those of stearic and oleic acids.[1] In $ZnSt_xOl_{(1-x)}$ it is clear from the DSC traces that a homogeneous solid solution is formed at all compositions.

X-ray Diffraction. The room-temperature powder X-ray diffraction patterns of $ZnSt_xOl_{(1-x)}$ ($0 \leq x \leq 1$) are shown in Figure 2a. For all compositions only 00*l* reflections are seen; this is due to the extremely high degree of preferred orientation arising as a consequence of the layered morphology of these compounds. In all compounds the 00*l* reflections could be indexed to a unique interlayer basal spacing. This is illustrated for $ZnSt_xOl_{(1-x)}$ ($x = 0.5$); the *d* spacing associated with each of the 00*l* reflections has been plotted against 1/*l* in Figure 2b. All points lie on a straight line, indicating the validity of the indexing and the fact that this material is characterized by a unique interlayer spacing.

There are two possible ways in which the layered ZnSt and ZnOl can organize to form a single-phase compound—they could form an interstratified structure, either regular or random, or a homogeneous solid solution. If the structure of $ZnSt_xOl_{(1-x)}$ was interstratified, a layer would have either all ZnSt molecules or all ZnOl molecules. The ZnSt and ZnOl layers could then be stacked either in a periodic regular fashion, for example, alternating ZnSt and ZnOl layers for the $ZnSt_{0.5}Ol_{0.5}$ composition, or stacked randomly. The former corresponds to regular interstratification and the latter to random interstratification. Regular interstratification would give rise to super lattice lines in the X-ray diffraction pattern.[15] Such an arrangement can be ruled out for the $ZnSt_xOl_{(1-x)}$ compounds; for no compositions are super structure reflections observed in the diffraction pattern (Figure 2a). Random interstratification, too, can be ruled out. The diagnostic criterion of a random interstratified structure is that it exhibits a nonintegral series of basal reflections,[15,16] that is, all spacings are not sub-multiples of a fundamental repeat distance, *d*(00*l*). As illustrated in Figure 2b, the observed 00*l* reflections in the $ZnSt_xOl_{(1-x)}$ compounds are sub-multiples of a unique interlayer spacing. Interstratification having been ruled out, the remaining arrangement is that where ZnSt and ZnOl components form a homogeneous solid solution. In such an arrangement, each layer would contain both ZnSt and ZnOl molecules in a molar ratio identical to that of the bulk. Support for such an arrangement is the fact that the interlayer spacing for $ZnSt_xOl_{(1-x)}$ compositions obey a one-dimensional form of Vegard's law, $d = xd_{(ZnSt)} + (1-x)d_{(ZnOl)}$, where *d* is the experimentally determined interlayer spacing of $ZnSt_xOl_{(1-x)}$, and $d_{(St)}$ and $d_{(Ol)}$ are the interlayer spacing of ZnSt and ZnOl. The values of the interlayer spacing for ZnSt and ZnOl are 42.7 and 41.8 Å, respectively. The linear variation of the interlayer spacing as a function of composition (Figure 2c) is clear evidence that $ZnSt_xOl_{(1-x)}$ forms a true solid solution over the entire composition range.

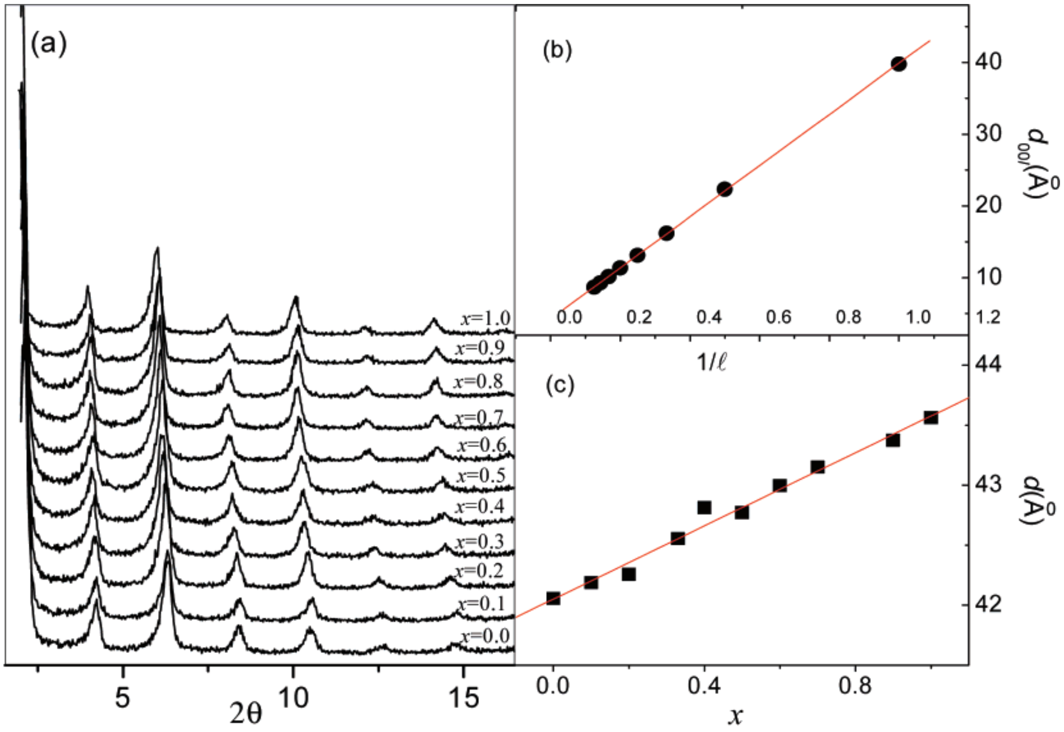

Figure 2. (a) Powder X-ray diffraction patterns for ZnSt$_x$Ol$_{(1-x)}$ at different compositions. (b) d_{00l} versus 1/l for ZnSt$_x$Ol$_{(1-x)}$, (x = 0.5) and (c) interlayer basal spacing of ZnSt$_x$Ol$_{(1-x)}$ at different compositions.

The DSC and diffraction measurements clearly establish that ZnSt and ZnOl can mix and form a homogeneous solid solution over the entire composition range with the interlayer repeat distance obeying a one-dimensional form of Vegard's law. In layered compounds, situations where Vegard's law, or deviations from it, are observed have been analyzed in terms of the rigidity of the layer.[17−20] It is in situations where the layers are flexible or "floppy" that the law is obeyed. In ZnSt$_x$Ol$_{(1-x)}$ the layers are flexible and could form a corrugated or pillbox-like arrangement to account for the presence of stearate and oleate molecules that are of different length. The average layer thickness would yield a normalized basal spacing that obeys Vegard's law.[17,18] However, the question of how the apparently linear stearate and bent oleate rodlike molecules are packed within a layer remains unanswered. To understand how the molecules are arranged and the conformational changes that occur on solid solution formation we have used infrared vibrational spectroscopy.

Infrared Spectroscopy. Vibrational spectroscopy, both infrared and Raman, has been used extensively to characterize organization and conformation in alkyl-chain assemblies.[21−23] In particular, the position of the symmetric and antisymmetric methylene stretching modes that appear between 2918 and 2848 cm^{-1} are sensitive to the conformation of the alkyl chain shifting to higher frequencies with increased conformational disorder.[24,25] This region is, however, not so informative for this system. The spectra of ZnSt$_x$Ol$_{(1-x)}$, in the methylene stretching region, for all compositions are almost identical to that of the end members. The methylene antisymmetric stretching mode appears at 2919 cm^{-1} and the symmetric stretching mode at 2848 cm^{-1}. These values indicate a fair degree of trans conformational order in the alkyl chains of solid solution.

The infrared spectra can also provide information on how the carboxylate group of the fatty acid is coordinated to zinc.[7] The difference in the positions of the carboxylate antisymmetric stretching and the symmetric stretching modes is indicative of the nature of metal−carboxylate coordination.[26] The carboxylate antisymmetric stretching and symmetric stretching modes are observed as intense bands at 1400 and 1542 cm^{-1} in ZnSt$_x$Ol$_{(1-x)}$, a difference of 142 cm^{-1}, for all compositions (see also Supporting Information). The observed difference of 142 cm^{-1} in ZnSt$_x$Ol$_{(1-x)}$ is characteristic of bridging bidentate coordination,[26] and the spectra indicate that there is no change in the nature of zinc−carboxylate coordination with composition.

In order to identify the changes in conformation of the stearate and oleate chains on solid solution formation, it is necessary to be able to distinguish features in the infrared spectra that are characteristic of each type of chain. This can be achieved, for example, if one of the chains, either stearate or oleate, is deutrated. An alternate, and perhaps easier, method in these compounds is to examine the progression bands in the infrared that are characteristic of the length of the all-trans chain/segment.

Infrared Progression Bands. The progression bands in the infrared arise from the coupling of vibrational modes of methylene units in trans registry and provide a quantitative measure of chain conformation. The coupling of CH$_2$ wagging (ν_3), twisting−rocking (ν_7), rocking−twisting (ν_8), and C−C skeletal stretch (ν_4) modes of all-trans segments in alkyl chains gives rise to a series of bands that are de-localized over the length of the all-trans segment and whose spacing and position depend on the number of coupled trans CH$_2$ units. Progression bands are analyzed by assigning to each band a wave-vector, k, which represents the phase angle or difference, ϕ_k, between adjacent oscillators, and which is related to the number, N, of contiguous all-trans methylene units.[27,28] It had been shown previously, from an assignment of the progression bands in the infrared (see also Supporting Information), that in ZnSt all 16 methylene units are in trans registry ($N = 16$), whereas in ZnOl the double bond effectively decouples these modes into two identical series, delocalized over two all-trans 7-CH$_2$ ($N = 7$) segments.[7,10]

The progression band region, 1100−1400 cm^{-1}, of ZnSt$_x$Ol$_{(1-x)}$ (Figure 3a) shows a larger number of bands as compared to that of either ZnSt ($N = 16$) or ZnOl ($N = 7$), indicating that

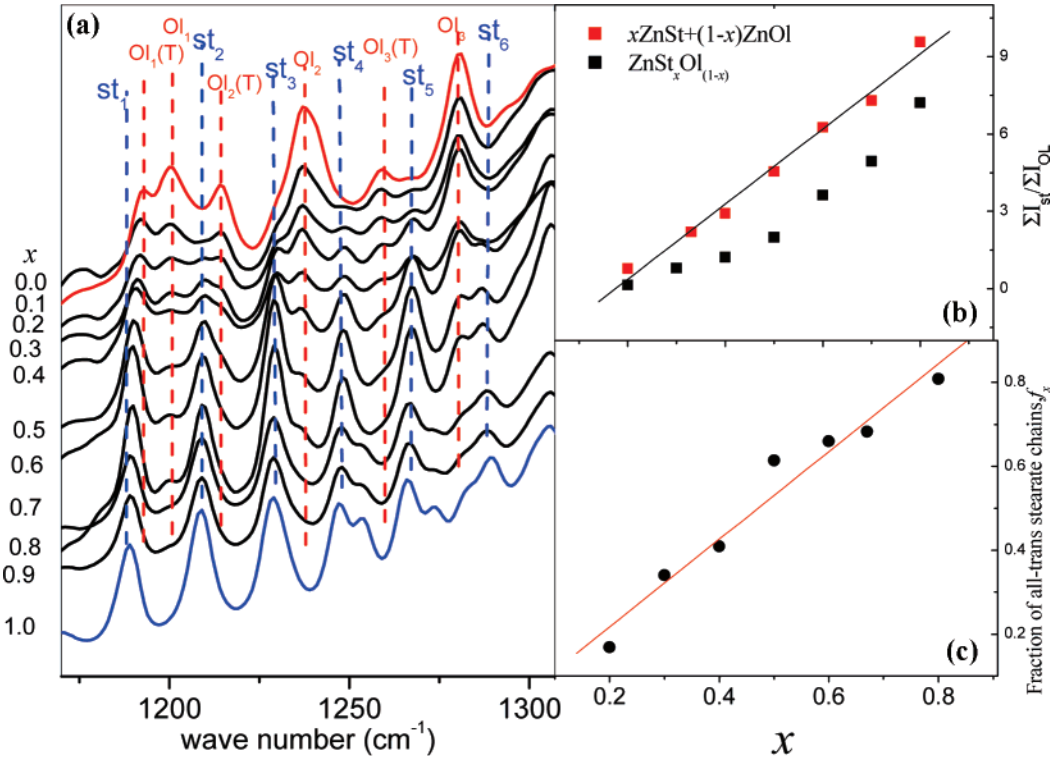

Figure 3. (a) Infrared spectra of $ZnSt_xOl_{(1-x)}$ in the wagging band progression region at different compositions. The spectrum of ZnSt is in blue and that of ZnOl in red. Stearate bands are labeled as St and oleate bands as Ol (b) the intensity ratio $\sum I_{(St)i}/I_{(Ol)}$ for $ZnSt_xOl_{(1-x)}$ and physical mixtures, xZnSt + $(1-x)$ ZnOl, at different compositions. (c) The fraction of stearate chains in $ZnSt_xOl_{(1-x)}$ that are all-trans for different compositions.

there could be two sets of progression bands with differing spacings. Two different progression series could be identified by assigning features in $ZnSt_xOl_{(1-x)}$ common to ZnSt with k values appropriate for a set of $N = 16$ coupled oscillators (labeled by the subscript St in Figure 3a.). The remaining bands appear at frequencies very similar to the progression bands of ZnOl and could therefore be assigned k values appropriate for a set of $N = 7$ coupled oscillators (see also Supporting Information). The features corresponding to the progression series for $N = 7$ are labeled with the subscript Ol in Figure 3a. Since features characteristic of ordered stearate ($N = 16$) and ordered oleate ($N = 7$) chains can be identified in the spectra of $ZnSt_xOl_{(1-x)}$, it is possible to obtain quantitative information regarding the concentration of each type of ordered chain.

The intensities of the progression bands assigned to St and Ol chains in the spectra of $ZnSt_xOl_{(1-x)}$ (Figure 3a) may be related to the molar ratio of all-trans stearate and oleate chains present in the solid solution.[29,30] This can be done from the ratio of the integrated intensities of selected bands corresponding to the different progression series of the St and Ol chains:

$$X_{(St)}/X_{(Ol)} = \kappa \sum I_{(St)i}/I_{(Ol)i} \tag{1}$$

where $X_{(St)}$ and $X_{(Ol)}$ are the molar concentrations of all-trans St and Ol chains, $I_{(St)i}$ and $I_{(Ol)i}$ are the integrated intensities of the wagging progression bands with $k = i$ of the stearate and oleate chains. The summation of the intensities is over a set of selected k values. The proportionality constant, κ, relates the intensity ratio to the molar concentration ratio. The proportionality constant was determined from the intensities of the progression band spectra of physical mixtures of ZnSt and ZnOl of known $X_{(St)}/X_{(Ol)}$ (see Supporting Information). In both ZnSt and ZnOl, it had been established that all chains are in all-trans registry at room temperature.[7,10] The wagging progression bands selected for determining the proportionality constant are the bands with $k = 1$, 2, 3, and 4 for the stearate chains and $k = 1$, 2, and 3 for the oleate chains.

The intensity ratio $I_{(St)i}/I_{(Ol)i}$ for $ZnSt_xOl_{(1-x)}$ and the physical mixtures are plotted as a function of composition in Figure 3b. It may be seen that for the physical mixture the ratio shows, as expected, a linear variation with composition. For the solid solution, however, the ratio is less than that of the corresponding physical mixture and is nonlinear. Figure 3b indicates there is increased disorder of the stearate chains in the solid solution as compared to the physical mixture. In principle, the ratio reflects changes in concentration of both ordered stearate and oleate chains in the solid solutions. However, when the intensities, $\sum I_{(Ol)i}$, for different compositions of $ZnSt_xOl_{(1-x)}$ were determined after normalizing the spectra with respect to the intensity of the C−H stretching mode, associated with the oleate double bond, that appears at 3008 cm^{-1}, it was found to be a constant. The C−H stretching mode associated with the double bond was chosen for normalization since it shows no change either in position or intensity with change in conformation. This was established by monitoring the band through the melting transition of ZnOl. The difference in the intensity ratio, $I_{(St)i}/I_{(Ol)i}$, of the solid solution and the physical mixture is, therefore, a measure of the decrease in concentration of all-trans stearate chains on formation of the solid solution.

In pure ZnSt, all stearate chains adopt an all-trans planar conformation at room temperature, while oleate chains in both ZnOl and $ZnSt_xOl_{(1-x)}$ are ordered at room temperature. It is, therefore, possible to determine the fraction, f_x^{St}, of stearate chains that are all-trans in $ZnSt_xOl_{(1-x)}$ at any composition from the ratio of the progression band intensity ratio of the solid solution with that of the physical mixture of the same composition, xZnSt + $(1-x)$ZnOl.

$$f_x^{St} = [\sum I_{(St)i}/I_{(Ol)i}]_{ZnStxOl(1-x)}/[\sum I_{(St)i}/I_{(Ol)i}]_{(xZnSt+(1-x)ZnOl)}$$

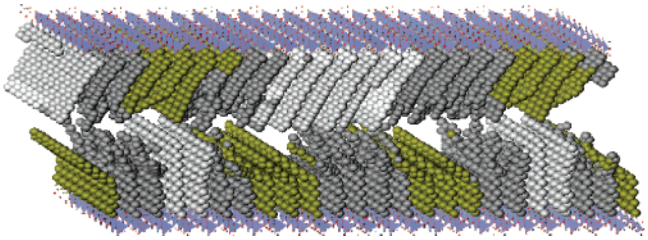

Figure 4. Schematic of single layer of $ZnSt_xOl_{(1-x)}$ of nominal composition $x = 0.6$. The oleate chains are shown in green, and the stearate chains are in gray. Stearate chains having gauche disorder are shaded darker.

This fraction, that is, the fraction of stearate chains in $ZnSt_xOl_{(1-x)}$ that are all-trans, has been plotted as a function of composition in Figure 3c. It can be seen that as the composition changes the fraction of stearate chains that are all-trans decreases with increasing oleate concentration, the variation being almost linear. This implies that that although the oleate chains retain their rigid bent rodlike structure, all stearate chains in $ZnSt_xOl_{(1-x)}$ do not retain a rigid linear geometry. The presence of a gauche defect would allow a stearate chain to adopt a bent structure. The formation of $ZnSt_xOl_{(1-x)}$ is, therefore, no longer a problem of how to accommodate rigid linear and bent rodlike molecules in a two-dimensional layer. It may be seen from Figure 3c that not all stearate chains in $ZnSt_xOl_{(1-x)}$ are disordered; some retain a rigid planar conformation. A single sheet of $ZnSt_xOl_{(1-x)}$ would, therefore, have oleate chains that are ordered, a fraction of the stearate chains, f_x^{St}, that are all-trans ordered, with the remaining stearate chains having at least one gauche defect. A schematic of a possible in-layer structure of $ZnSt_xOl_{(1-x)}$ is shown in Figure 4. The average layer thickness for such an arrangement would show a linear variation with composition and would explain why the interlayer basal spacing obeys Vegard's law.

Relating Conformational Disorder with Enthalpy of Melting. Increase in temperature induces conformational disorder in the chains. The presence of a single gauche bond in an all-trans ordered chain/segment is sufficient to decouple the vibrational modes, and such chains/segments no longer contribute to the intensity of the progression bands. The intensity of the progression bands is, therefore, directly proportional to the concentration of all-trans chains in the ensemble. It has been shown previously that melting in ZnSt and ZnOl is associated with the total disappearance of all-trans chains/segments, as inferred from the absence of progression bands at melt.[7,10] A similar situation exists in the solid solutions. The wagging progression bands of $ZnSt_xOl_{(1-x)}$ ($x = 0.5$) at different temperatures are shown in Figure 5. It may be seen that melting is characterized by the complete disappearance of progression bands due to all-trans chains of stearate and the trans 7-CH_2 segments of the oleate.

If it is assumed that only all-trans stearate chains and trans 7-CH_2 oleate segments contribute significantly to the enthalpy of melting and that disordered chains/segments do not (a disordered chain/segment is defined as having one or more gauche bonds), it is possible to estimate the enthalpy of the melting transition from the fraction of stearate chains in $ZnSt_xOl_{(1-x)}$ that are all-trans ordered at room temperature, as estimated from the infrared progression band intensities (Figure 3c):

$$\Delta H = x\Delta H_{(ZnSt)} f_x^{St} + (1-x)\Delta H_{(ZnOl)} \qquad (2)$$

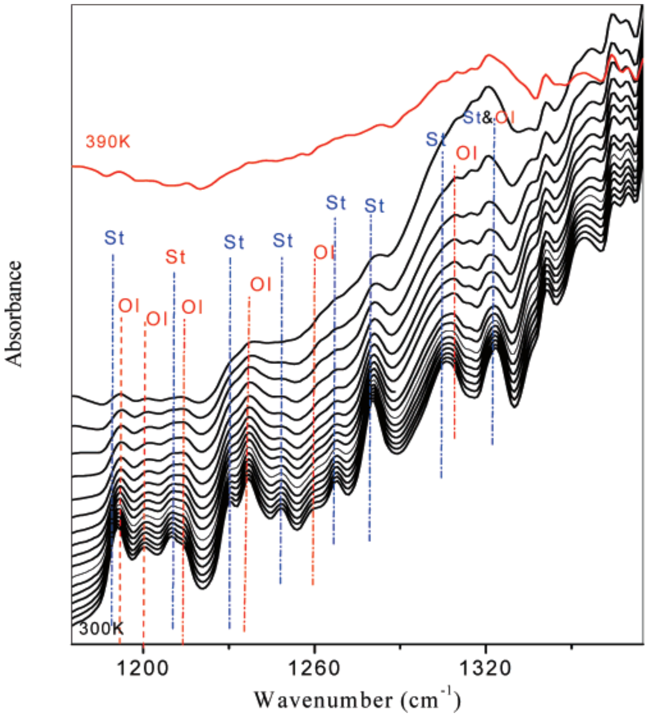

Figure 5. Wagging progression bands in the infrared spectra of $ZnSt_xOl_{(1-x)}$, $x = 0.5$, at different temperatures. The spectrum at melt (390 K) is shown in red.

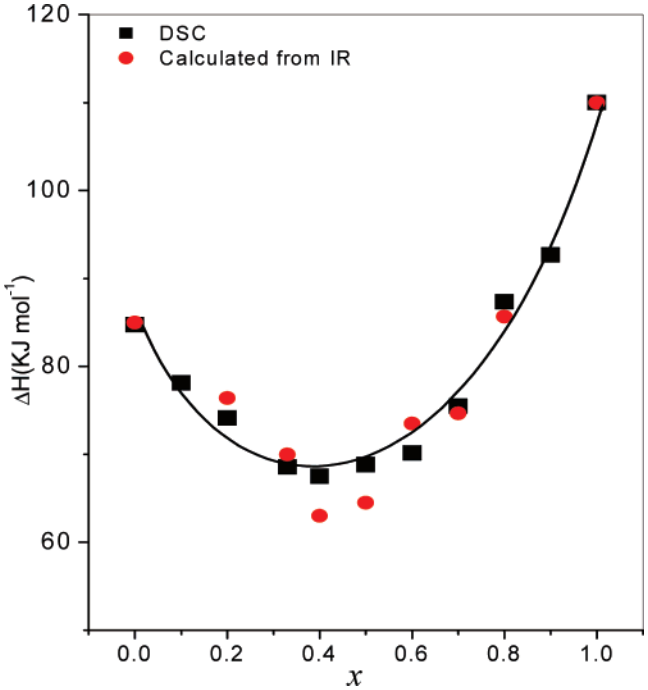

Figure 6. Comparison of the enthalpy of melting of $ZnSt_xOl_{(1-x)}$ calculated from the infrared data with the experimental DSC values (the line is a guide to the eye).

where f_x^{st} is the fraction of stearate chains in $ZnSt_xOl_{(1-x)}$ that are all-trans at room temperature; $\Delta H_{(ZnSt)}$ and $\Delta H_{(ZnOl)}$ are the enthalpy of melting of pure ZnSt and ZnOl, and their values are 115 and 80 KJ mol^{-1}, respectively. (The oleate chains in both ZnOl and $ZnSt_xOl_{(1-x)}$ are completely ordered at room temperature, i.e., $f_x^{Ol} = 1$.) The ΔH values calculated using the above equation have been compared with DSC-determined values for different compositions of $ZnSt_xOl_{(1-x)}$ in Figure 6. It may be seen that the values are close and that the calculated ΔH values show the same variation with composition as the experimentally determined DSC values. The close coincidence indicates that the estimates of the concentration of ordered stearate chains in $ZnSt_xOl_{(1-x)}$ (Figure 3c) are reasonable and that the assumption that only all-trans stearate chains and trans 7-CH_2 oleate segments contribute to the enthalpy of melting is not too drastic.

Conclusion

The zinc salts of the linear saturated stearic acid and the bent mono-unsaturated oleaic acid form solid solutions over the entire composition range. This was established by X-ray diffraction as well as DSC measurements. The melting temperature of $ZnSt_xOl_{(1-x)}$ shows a linear variation with composition. The enthalpy of melting, however, does not show this trend and has a minimum at a composition with $x = 0.4$. X-ray diffraction rules out a structural organization of the layered $ZnSt_xOl_{(1-x)}$ in which ZnSt and ZnOl layers are interstratified in either a regular or random fashion. Instead, it indicates that both stearate and oleate chains are present in the same layer with molar ratio identical to the bulk and with the interlayer spacing, d, obeying a one-dimensional form of Vegard's law, $d = xd_{(\mathrm{ZnSt})} + (1-x)d_{(\mathrm{ZnOl})}$.

Infrared spectroscopy tells us how the ZnSt and ZnOl are packed in a layer. Part of the ZnSt molecules present in $ZnSt_xOl_{(1-x)}$ are conformationally disordered. The presence of a gauche bond would allow these stearate chains to adopt bent structures; the formation of $ZnSt_xOl_{(1-x)}$ is, therefore, no longer a problem of how to mix rigid linear and bent rodlike molecules. The concentration of conformationally disordered stearate chains increases with oleate concentration in $ZnSt_xOl_{(1-x)}$. Quantitative estimates of this concentration were obtained from a comparison of the intensities of the progression bands in the infrared spectrum of $ZnSt_xOl_{(1-x)}$ with that of physical mixtures of ZnSt and ZnOl wherein all chains adopt an all-trans conformation. The progression bands arise from a coupling of vibrational modes of methylene units in trans registry and provide a characteristic signature to distinguish between all-trans ordered stearate and oleate chains in the infrared. The enthalpy of the melting transition of $ZnSt_xOl_{(1-x)}$ was estimated from the fraction of stearate chains in $ZnSt_xOl_{(1-x)}$ that are all-trans ordered and the assumption that only all-trans stearate and oleate chains contribute to the enthalpy. The estimated values were close to the DSC-determined enthalpy values and were able to reproduce the observed experimental variation with composition. In the $ZnSt_xOl_{(1-x)}$ system we have thus been able to establish a quantitative relation between molecular conformational order and the thermodynamic enthalpy of melting of the ensemble.

The question then arises as to why stearic acid and oleic acid do not form a solid solutions or why a situation similar to that described here is not observed in LB films of stearic and oleic acids or even stearic and elaidic acids. The answer is in the crucial role played by zinc coordination. Coordination to zinc keeps the layer intact while allowing a greater distance between chains as compared to the corresponding fatty acids. In zinc stearate, the interchain distance is 4.69 Å, which is the Zn−Zn distance in the layer, while in stearic acid it is 3.7 Å. The larger volume available to the alkyl chains in these zinc soaps permits them a much greater degree of conformational freedom. As a consequence, stearate and oleate chains can mix in a random homogeneous fashion to form $ZnSt_xOl_{(1-x)}$ solid solutions.

Supporting Information Available: (1) Table of the melting temperature (T_m), and enthalpy change, ΔH (KJ mol^{-1}), of $ZnSt_xOl_{(1-x)}$ at different compositions. (2) Infrared spectra of the solid solution $ZnSt_xOl_{(1-x)}$ in the carboxylate stretching region for different compositions. (3) Progression bands in the infrared spectra of ZnSt and ZnOl and the dispersion of the band frequencies. (4) Table of observed peak positions and assignments of the infrared progression bands of ZnSt and ZnOl. (5) Table of observed peak positions of the methylene wagging band progression series in the infrared spectra of $ZnSt_xOl_{(1-x)}$ and their assignment. (6) Infrared spectrum in the wagging band progression region, 1100−1400 cm^{-1}, of physical mixtures of ZnSt and ZnOl, xZnSt + $(1-x)$ZnOl, at different molar ratios. This material is available free of charge via the Internet at http://pubs.acs.org.

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