THE JOURNAL OF
PHYSICAL
CHEMISTRY B
LETTERS

2006, *110,* 651−654
Published on Web 12/18/2005

Contrasting Melting Behavior of Zinc Stearate and Zinc Oleate

S. Barman[†] **and S. Vasudevan***[,†,‡]

Solid State and Structural Chemistry Unit and Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Received: October 11, 2005; In Final Form: December 1, 2005

The influence of a double bond in the middle of an otherwise flexible hydrocarbon chain on the melting of such assemblies has been investigated by comparing the melting behavior of zinc stearate and zinc oleate. By monitoring features in the infrared spectra that are characteristic of the global conformation of the hydrocarbon chain, it is shown that the double bond 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 independent events.

Unsaturated fatty acids are widely distributed in nature, being one of the main constituents of cell membranes. The presence of the double bond is known to enhance fluidity and control phase transition behavior and functionality of membranes.[1] Chain unsaturation can have dramatic consequences on the melting of lipid bilayers. A single double bond in a *cis* configuration can result in a significant downward shift of the melting temperature with the effect being maximal when the double bond is at the center of the chain.[2] Here, we explore how the presence of a single rigid link in the middle of an otherwise flexible chain affects the thermal evolution of conformational disorder of the chain and hence the melting of the hydrocarbon assembly. We have compared the melting behavior of zinc stearate and oleate (*cis*-9-octadecenoate) using X-ray diffraction (XRD), differential scanning calorimetry (DSC), and infrared spectroscopy.

The title compounds were chosen for this study because zinc stearate, unlike most other polyvalent metal soaps, is known to pass directly from the solid to liquid phase at 403 K, without any intermediate mesophases.[3] Although crystal structures of zinc stearate and oleate have not been reported, on the basis of X-ray absorption and infrared spectroscopic studies[4] and from reported structures of zinc soaps with shorter hydrocarbon chains,[5] it is reasonable to conclude that these compounds, too, have a layer structure with tetrahedrally coordinated zinc cations connected by carboxylate bridges to four stearate/oleate chains. Upon melting, the coordination of the carboxylate to zinc changes from bridging bidentate to one that has considerable monodentate character, resulting in breaking up of the inorganic sheets.[3] Metal coordination plays an important role in the thermal stability of these compounds. Both zinc stearate and zinc oleate are solids at room temperature with melting points considerably higher than the corresponding fatty acid. Coordination also defines the closest interchain distance in the soap, 4.69 Å, which is the Zn−Zn distance in the layer. In the corresponding fatty acids, this distance is 3.7 Å; packing considerations are, therefore, likely to be less important in the soap.

The zinc soaps were prepared by the addition of aqueous solutions of the sodium salt of the fatty acid to $ZnCl_2$ solution. The interlayer spacing of zinc stearate, as determined from powder XRD, is 42.7 Å. From the variation of the interlayer spacing with hydrocarbon chain length (see the Supporting Information), it was concluded that the hydrocarbon chains are arranged as tilted bilayers with a tilt angle of 27°. The interlayer spacing for zinc oleate is 41.8 Å, which is little over twice the end-to-end distance of the oleate chains, 19.4 Å.

Zinc stearate showed a single reversible exothermic transition at 403 K in the DSC trace, whereas the oleate shows two transitions, at 357 and 373 K (Figure 1a). Variable temperature XRD measurements (see the Supporting Information) showed that the transition at 357 K in zinc oleate is associated with an increase in the interlayer separation from 41.8 to 43.1 Å (Figure 1b). At 373 K, the sample melts and Bragg peaks are no longer seen in the XRD. In zinc stearate, on the other hand, the interlayer spacing stays constant up to the melt, 403 K.

Vibrational spectroscopy has been widely used to monitor conformation and its changes in alkyl chain assemblies.[6,7] The positions of the methylene symmetric, $\nu_{sym}(CH_2)$, and asymmetric, $\nu_{asym}(CH_2)$, modes are known to shift to higher frequencies with increased conformational disorder.[8,9] For an all-*trans* alkyl chain, as in the case of crystalline *n*-alkanes, the symmetric and antisymmetric stretching frequencies are in the range 2846−2850 and 2916−2920 cm^{-1}, respectively. With increasing number of gauche conformers, as in the high temperature liquid phases of the *n*-alkanes, the range shifts to 2855−2865 and 2925−2935 cm^{-1}, respectively. In the zinc stearate and oleate, too, similar changes in the position of the CH_2 stretching modes are observed upon melting (see the Supporting Information). At room temperature, the positions of the symmetric, $\nu_{sym}(CH_2)$, and asymmetric, $\nu_{asym}(CH_2)$ modes, 2848 and 2926 cm^{-1}, respectively, are characteristic of conformationally ordered alkyl chains. At melt, there is an abrupt change to higher frequencies, 2860 and 2931 cm^{-1}, respectively. These values are typical of disordered hydrocarbon chains.

---

* Corresponding author. E-mail: svipc@ipc.iisc.ernet.in.
[†] Solid State and Structural Chemistry Unit.
[‡] Department of Inorganic and Physical Chemistry.

10.1021/jp055814m CCC: $33.50

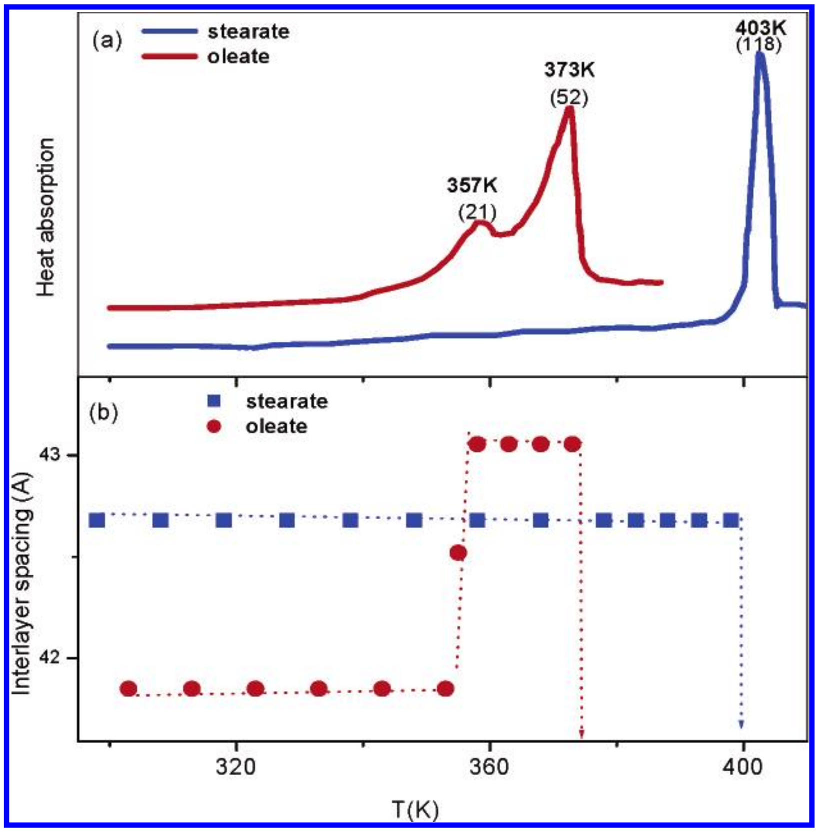


Figure 1. (a) DSC traces for zinc stearate and zinc oleate. The transition temperatures and the enthalpy values (in parentheses) in kilojoules per mole are indicated. (b) Temperature dependence of the interlayer spacing of zinc stearate and zinc oleate.

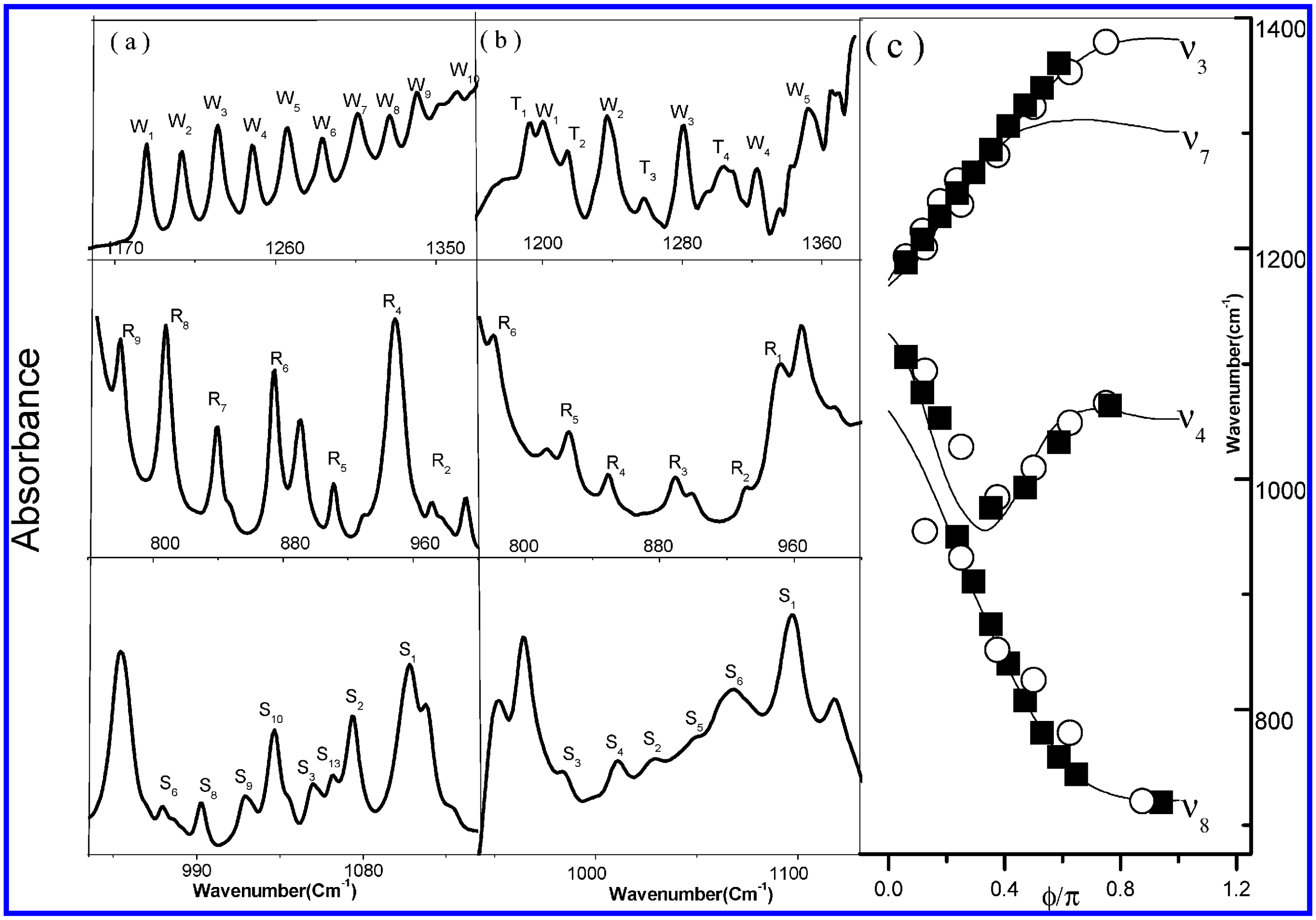


Figure 2. Methylene wagging (ν_3,W_k), twisting−rocking (ν_7,T_k), rocking−twisting (ν_8,R_k), and C−C stretch (ν_4,S_k) progression bands in the infrared spectrum of (a) zinc stearate and (b) zinc oleate. (c) Dispersion of the progression bands for zinc stearate (■) and zinc oleate (○). The solid line is the calculated dispersion curve for an infinite polymethylene chain.[11,12]

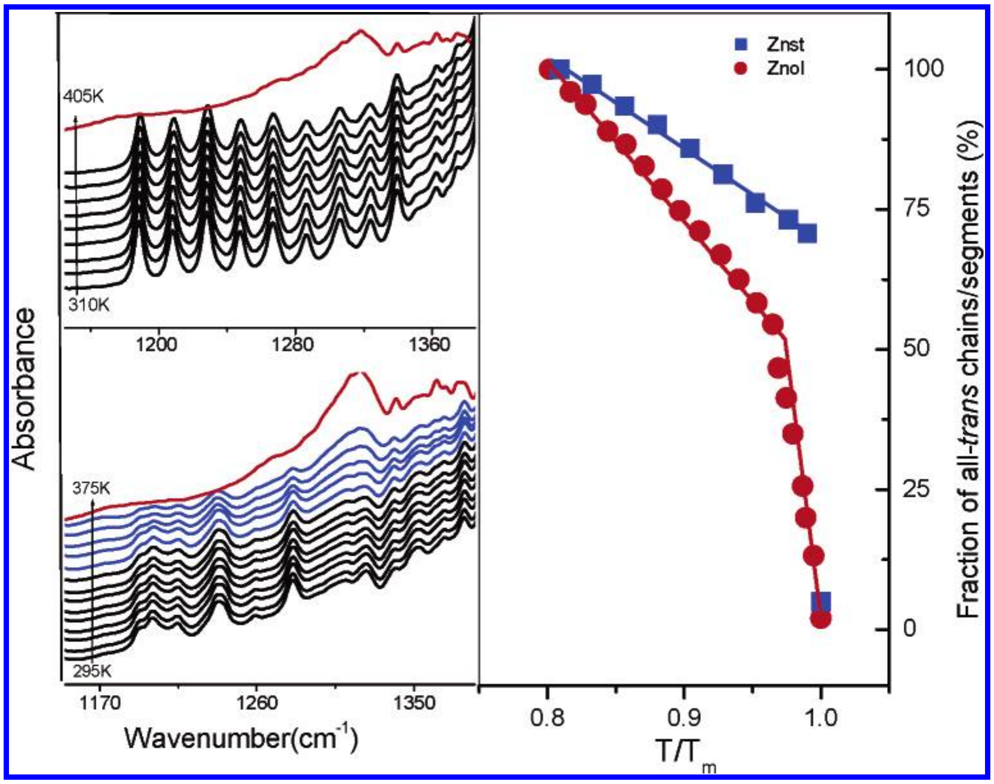
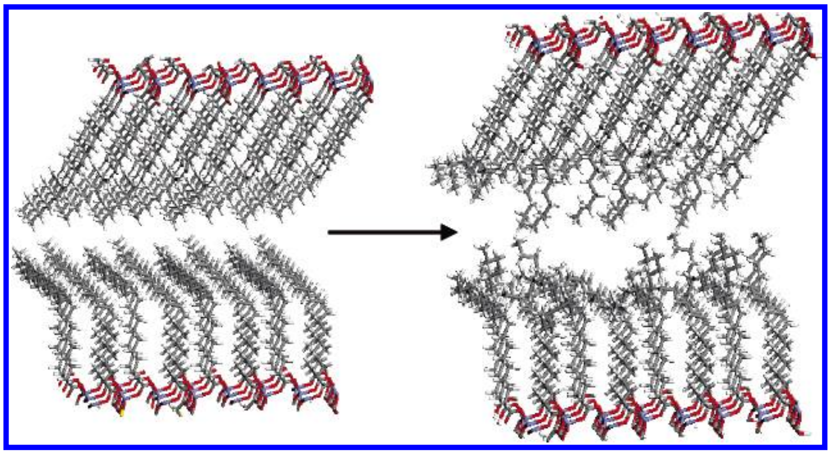


Figure 3. Methylene wagging progression bands recorded at different temperatures for (a) zinc stearate and (b) zinc oleate The spectrum at melt is shown in red and above the 357 K transition of the oleate in blue. (c) Thermal variation of the fraction of all-*trans* methylene chains in zinc stearate and the fraction of *trans*-7-CH_2 segments in zinc oleate (T_m is the melting temperature).

SCHEME 1



Here, we use the intensities of the progression bands in the infrared that arise from the coupling of the vibrational modes of methylene units in *trans* registry as 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 gives rise to a series of bands that are delocalized 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 a wave vector, k, which represents the phase angle or difference, ϕ_k, between adjacent oscillators, to each band in the spectrum.[10−12] The phase difference is given by $\phi_k = k\pi/(N + 1)$ ($k = 1, 2, ..., N$), where N is the number of coupled *trans*-CH_2 units. When correctly assigned, a smooth dispersion curve is obtained for a plot of ν_k versus ϕ_k. For zinc stearate and oleate, smooth dispersion curves are obtained when the number of coupled *trans*-CH_2 units considered in the assignment of the progression band spectra (Figure 2a and b) is 16 and 7, respectively (Figure 2c) (see also the Supporting Information). For both compounds, the dispersions for a particular mode lie on identical curves, which is the same as that calculated for an infinite polymethylene chain. The progression band assignment indicates that in zinc stearate all 16 methylene units are in *trans* registry, whereas in zinc oleate the double bond effectively decouples these modes into two identical series, delocalized over two all-*trans* 7-CH_2 segments.

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 and the ratio of the integrated intensities of the progression bands at two temperatures, a direct measure of the ratio of the concentration of all-*trans* chains at the two temperatures. The wagging progression bands of zinc stearate and oleate at different temperatures are shown in parts a and b of Figure 3, respectively. It may be seen that melting is characterized by the total disappearance of progression bands due to all-*trans* chains of zinc stearate and the *trans*-7-CH_2 segments in the oleate. In both compounds, all hydrocarbon chains are present in the ordered all-*trans* state at room temperature. The ratio of the integrated intensity of the progression bands at any temperature with respect to that at room temperature is the fraction of the all-*trans* chains present in the sample at that temperature. Figure 3c shows that in zinc stearate melting occurs when ∼30% of the chains are disordered. Any increase in the concentration of disordered chains results in breaking up of the zinc stearate structure. In zinc oleate, in comparison, melting occurs in two steps. At the first transition, 357 K, roughly half of the *trans*-7-CH_2 segments present are disordered and at melt the remaining half. This suggests that at the first transition only the *trans*-7-CH_2 segments that are toward the methyl side of the double bond of the oleate chains are disordered (Scheme 1), with the increased disorder being accommodated by the increase in interlayer spacing (Figure 1). Melting occurs only when *all* of the remaining *trans*-7-CH_2 segments are disordered, in contrast to what occurs in zinc stearate where disordering of ∼30% of the chains is sufficient to induce melting. The zinc oleate structure can accommodate a much larger concentration of disordered chains as compared to the stearate. In conclusion, we have shown that the presence of a double bond, or rigid link, in the middle of a hydrocarbon chain decouples the thermal evolution of conformational disorder in the two segments and the melting of such assemblies occurs as two independent events.

Supporting Information Available: (1) X-ray diffraction patterns of saturated fatty acid zinc soaps as a function of chain length, (2) X-ray diffraction patterns of zinc stearate and oleate at different temperatures, (3) methylene stretching modes in the infrared spectrum of zinc stearate at different temperatures, and (4) assignments of the infrared progression bands in zinc stearate and oleate. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Stryer, L. *Biochemistry*, 3rd ed.; Freeman: San Francisco, CA, 1974; pp 247−249.

(2) Chapman, D. In *Biomembranes*; Shinitzky, M., Ed.; VCH: Weinheim, Germany, 1993.

(3) Akanni, M. S.; Okoh, E. K.; Burrows, H. D.; Ellis, H.A. *Thermochim. Acta* **1992**, *208*, 1.

(4) Ishioka, T.; Maeda, K.; Watanabe, I.; Kawauchi, S.; Harada, M. *Spectrochim. Acta, Part A* **2000**, *56*, 1731.

(5) Lacouture, F.; Peultier, J.; Francois, M.; Steinmetz, J. *Acta Crystallogr.* **2000**, *C56*, 556.

(6) Zerbi, G.; Del Zoppo, M. In *Modern Polymer Spectroscopy*; Zerbi, G., Ed.; Wiley-VCH: Weinheim, Germany, 1999.

(7) Venkataraman, N. V.; Vasudevan, S. *J. Phys. Chem B* **2002**, *106*, 7766.

(8) MacPhail, R. A.; Straus, H. L.; Snyder, R. G.; Elliger, C. A. *J. Phys. Chem.* **1984**, *88*, 334.

(9) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145.

(10) Snyder, R. G. *J. Mol. Spectrosc.* **1960**, *4*, 411.

(11) Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1963**, *19*, 85.

(12) Tasumi, M.; Shimanouchi, T.; Miyazawa, Y. *J. Mol. Spectrosc.* **1962**, *9*, 261.