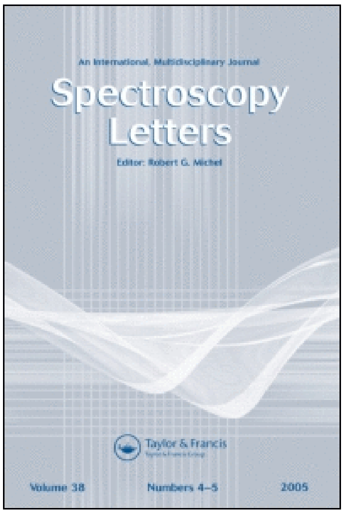

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Ftir Studies on Phase Transitions of *N*-Octadecanoyl-L-Alanine and Zinc Octadecanoyl-L-Alaninate Lb Films

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FTIR STUDIES ON PHASE TRANSITIONS OF *N*-OCTADECANOYL-L-ALANINE AND ZINC OCTADECANOYL-L-ALANINATE LB FILMS

KEY WORDS: Variable temperature FTIR, *N*-Octadecanoyl-L-alanine, Zinc, Hydrogen bond, Phase transition.

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ABSTRACT

The phase transitions of *N*-octadecanoyl-L-alanine and zinc octadecanoyl-L-alaninate LB films have been investigated through variable temperature FTIR spectroscopy. Hydrogen-bonding interactions between the enantiomeric head-groups strengthens the interactions between the alkyl chains so that the transition temperature of the *N*-octadecanoyl-L-alanine LB film (T_c = 122 °C) is nearly twice as high as that of the same-chain-length stearic acid LB film (T_c = 65 °C).

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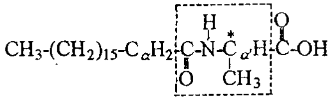
The intermolecular hydrogen-bonding interactions in the zinc octadecanoyl-L-alaninate LB film are greatly intensified in comparison to that in the *N*-octadecanoyl-L-alanine LB film; the relatively weak hydrogen-bonding interaction in the latter is easily disrupted around its transition temperature (T_c = 122 °C) together with an abrupt increase of $\nu_a(CH_2)$ stretching frequency, while the intensified intermolecular hydrogen-bonding interaction in the former weakens step by step with temperature along with a monotonic increase of $\nu_a(CH_2)$ stretching frequency, the zinc octadecanoyl-L-alaninate LB film thus exhibits a different phase behavior from the pure enantiomer LB film. Therefore, the strength of the intermolecular hydrogen bond is closely related to the interchain interaction and the film phase behavior.

1. INTRODUCTION

The previous paper reports the chirality of the *N*-octadecanoyl-L-alanine LB film in which the chiral molecules assemble regularly to develop an extended intermolecular hydrogen-bonding network. The hydrogen-bonding effect strengthens the interchain interaction and results in a dense chain packing accordingly.[1] Phase transition is one of fundamental physicochemical properties of LB films, thus it is significant to study the influence of hydrogen bond upon the phase behaviors of the films. In the present work, variable temperature FTIR spectroscopy is employed to investigate the phase transitions of 11-monolayer *N*-octadecanoyl-L-alanine and zinc octadecanoyl-L-alaninate LB films. The intermolecular hydrogen-bonding interaction increases the transition temperature of film, and a further intensified hydrogen-bonding interaction leads to the occurrence of a different phase behavior.

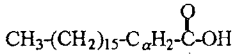
2. EXPERIMENTAL

The synthesis of *N*-octadecanoyl-L-alanine sample [FIG. 1 (a)] and the fabrication method of 11-monolayer Y-type LB films from pure water and Zn^{2+}-



$$CH_3\text{-}(CH_2)_{15}\text{-}C_{\alpha}H_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}\overset{H}{N}\text{-}\overset{*}{\underset{CH_3}{C_{\alpha'}}}H\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

(a)



$$CH_3\text{-}(CH_2)_{15}\text{-}C_{\alpha}H_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

(b)

FIG. 1. Chemical structures of amphiphiles, (a) *N*-octadecanoyl-L-alanine, and (b) stearic acid.

containing subphases were the same as those described previously.[1] The pH values of pure water and Zn^{2+}-containing subphases were ~ 6.0 and 6.8, respectively. The film was deposited at a fixed surface pressure 40 mN/m.

FTIR spectra were recorded on a Bruker IFS 66V spectrophotometer equipped with a DTGS detector. The infrared spectra were obtained by collecting 1000 scans at a resolution of 4 cm^{-1}. The film spectrum was obtained by subtraction of the CaF_2 spectrum from the sample spectrum. Before the measurement of the film spectra at elevated temperatures, the film-deposited CaF_2 plate was mounted on a *SPECAC* heating cell, and the temperature control was achieved by a copper-constantan thermocouple with an accuracy of ± 1 °C. After the sample was heated to the desired temperature, 15 min was spent for a thermal equilibration, then the temperature-dependent film spectra were recorded.

3. RESULTS AND DISCUSSION

3. 1. FTIR Characterization of N-Octadecanoyl-L-alanine and Zinc Octadecanoyl-L-alaninate LB Films

FIG. 2 shows the FTIR spectra of 11-monolayer *N*-octadecanoyl-L-alanine (a) and zinc octadecanoyl-L-alaninate (b) LB films in the regions of 3400–2800 and 1800–1100 cm^{-1}. In FIG. 2 (a), two strong absorption bands at 2918 and

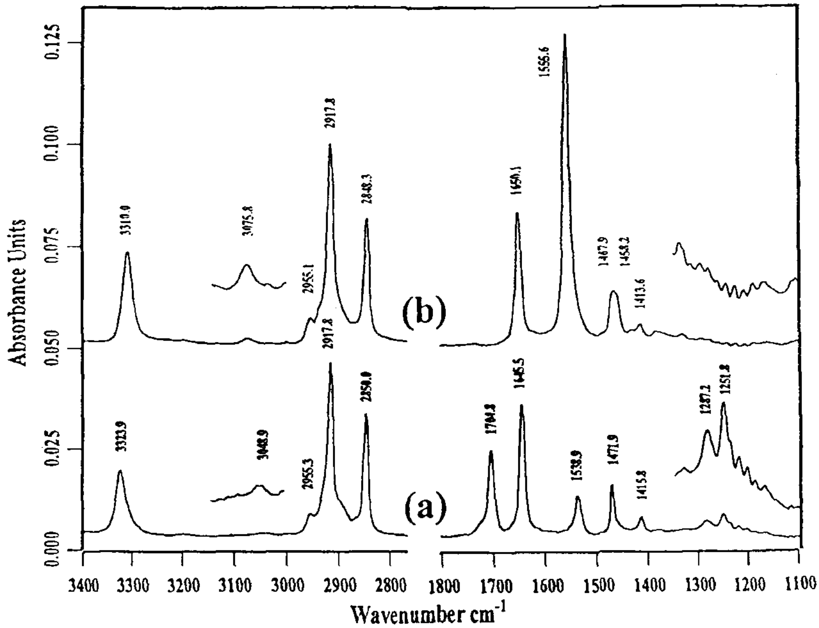


FIG. 2. FTIR spectra in the 3400–2800 and 1800–1100 cm^{-1} regions of 11-monolayer LB films of, (a) *N*-octadecanoyl-L-alanine, and (b) zinc octadecanoyl-L-alaninate.

2850 cm^{-1} are assigned to the antisymmetric and symmetric CH$_2$ stretching vibrations [$\nu_a(CH_2)$, $\nu_s(CH_2)$] respectively, indicating that the alkyl chains in the film take highly ordered *all-trans* conformations.[2] A singlet at 1472 cm^{-1} is due to the CH$_2$ scissoring mode [$\delta(CH_2)$], which is very sensitive to the interchain interaction.[3] This peak position indicates that the alkyl chains take a triclinic subcell structure where the chains are packed in parallel arrangement.[3] A weak band at 1415 cm^{-1} is attributed to the bending modes of the $C_\alpha H_2$ groups adjacent to amide groups[4] and the C_α·H groups relevant to the chiral centers [seen FIG. 1 (a)].

The 1705-cm^{-1} band is assigned to the C=O stretching vibrations of carboxylic group dimers.[1] A series of absorption bands in the 1300–1100 cm^{-1} region are due to the CH_2 band progression arising from the CH_2 wagging vibrations [$\omega(CH_2)$] of the *trans* hydrocarbon chains.[5] The presence of the band progression as well-resolved peaks is a clear indicator of close packing of the alkyl chains in the film. It is known that in the stearic acid LB film the coupled mode of C–O stretching and O–H in-plane bending vibrations [ν(C–O) + δ(O–H)] is positioned at approximately 1300 cm^{-1},[6] but due to the effects of amide groups and chiral carbons on the carboxylic groups, the corresponding band shifts to 1252 cm^{-1} in the *N*-octadecanoyl-L-alanine LB film. In FIG. 2 (b) for a zinc *N*-octadecanoyl-L-alaninate LB film, the disappearance of the 1252-cm^{-1} band implies that the band assignment is reliable.

In FIG. 2 (a), three absorption bands at 3324, 1646, and 1538 cm^{-1} are assigned to amide A [ν(N–H)], amide I [ν(C=O)], and amide II [δ(N–H)] bands, respectively,[1] and a very weak peak around 3050 cm^{-1} is due to amide B band arising from first harmonic of δ(N–H) mode.[7] In case of the unassociated state, the ν(N–H) frequency appears around 3450 cm^{-1}, and the amide II band at 1510 cm^{-1}.[7] Generally, the ν(N–H) frequency lower than 3330 cm^{-1} indicates that the amino acid residues in the amphiphiles are engaged in hydrogen bond.[9] The amide A [ν(N–H)] and amide II [δ(N–H)] band frequencies in FIG. 2 (a) shift respectively to lower and higher wavenumbers as compared with those in the unassociated state, which suggests the occurrence of the hydrogen-bonding interactions between the chiral headgroups in the film. The enantiomeric amphiphiles arrange regularly in a definite direction, and the neighboring molecules twist each other to develop the chirality of two-dimensional aggregate.[1]

FIG. 2 (b) is the FTIR spectrum of the zinc octadecanoyl-L-alaninate LB film deposited from Zn^{2+}-containing subphase. Compared with FIG. 2 (a) in the same region, the 1705-cm^{-1} C=O stretching band of the carboxylic acid dimers completely disappears, instead, a very strong band at 1556 cm^{-1} occurs and is assigned to the antisymmetric carboxylate stretching vibration [ν_a(COO)]. Accordingly, the ν(N–H) peak position is shifted down to 3310 cm^{-1} in comparison with the 3324 cm^{-1} position in the octadecanoyl-L-alanine LB film, and amide B band (first harmonic of N–H in-plane bend) is shifted up to 3075 cm^{-1} from 3050 cm^{-1}. These changes indicate that the hydrogen-bonding interactions between the zinc octadecanoyl-L-alaninate molecules are greatly intensified. At the same time, the $\nu_s(CH_2)$ frequency is reduced to 2848 cm^{-1} from 2850 cm^{-1} along with the increased $\nu(CH_2)$ band intensities, indicative of a tight packing arrangement of the alkyl chains. This indicates that the enhanced interactions between the hydrophilic headgroups can improve the assembly features of the corresponding hydrophobic chains.

Two bands with comparable intensities are overlapped in the 1470–1450 cm^{-1} region in FIG. 2 (b), and the corresponding second derivative spectrum shows that the two peaks are positioned at 1468 and 1458 cm^{-1}, respectively (not shown). The 1468-cm^{-1} singlet band is due to the CH_2 scissoring vibration, indicating that the alkyl chains take a hexagonal subcell packing in the salt form,[3] and the other band at 1458 cm^{-1} is attributed to the symmetric carboxylate stretching vibration [ν_s(COO)], which is consistent with the assignment of the ν_s(COO) band (1456 cm^{-1}) of solid zinc acetate.[9] The spectral features of the film here is similar to those of the cobalt stearate LB film, where the ν_s(COO) and $\delta(CH_2)$ bands were positioned at 1456 and 1468 cm^{-1}, the alkyl chains took the hexagonal subcell packing with the chain perpendicular to the film normal.[10] This indicates that the zinc octadecanoyl-L-alaninate film possesses a comparable structure to that of the cobalt stearate film, i.e., Zn^{2+} ions enter into the dimer rings of carboxylic acid groups. The electrostatic interactions between Zn^{2+}

ions and carboxylates are stronger than the interaction in the carboxylic acid dimers, thus giving rise to an enhanced hydrogen-bonding interactions between the amide groups.

The above results indicate that the hydrogen-bonding interactions between the headgroups in the salt form are enhanced due to the condensation effect of Zn^{2+} ions, which results in intensified interactions between the alkyl chains. The chain packing is transformed from the triclinic subcell containing a single enantiomer to a hexagonal one containing a complexed molecule. These structural changes would give rise to the variation of the fundamental physicochemical properties, such as phase transition, of LB films.

3. 2 Variable Temperature FTIR Spectra of N-Octadecanoyl-L-alanine LB Film

FIG. 3 shows the variable temperature FTIR spectra of a 11-monolayer *N*-octadecanoyl-L-alanine LB film in the C–H stretching region at elevated temperatures (30–130 °C). Two strong bands at 2918 and 2850 cm^{-1} in the spectrum of 30 °C are due to the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ respectively. The two band frequencies almost remain unchanged up to 110 °C with temperature, then increase abruptly to 2924 and 2854 cm^{-1} in the temperature range 120–125 °C, and nearly keep constant above 125 °C. The $\nu(CH_2)$ frequencies are sensitive to the conformations of hydrocarbon chains,[2] the values of 2918 and 2850 cm^{-1} for the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ bands are characteristic of the *all-trans* conformations of highly ordered alkyl chains, and the values of 2924 and 2854 cm^{-1} are indicative of a liquid-crystalline state with the population of *gauche* conformations. Simultaneously, the $\nu_a(CH_2)$ band intensity decreases gradually together with a broadened bandwidth, and the intensity reduces remarkably in the temperature range of 120–125 °C while the bandwidth broadens progressively. Previous research pointed out that the $\nu(CH_2)$ bandwidths reflected the mobility of the

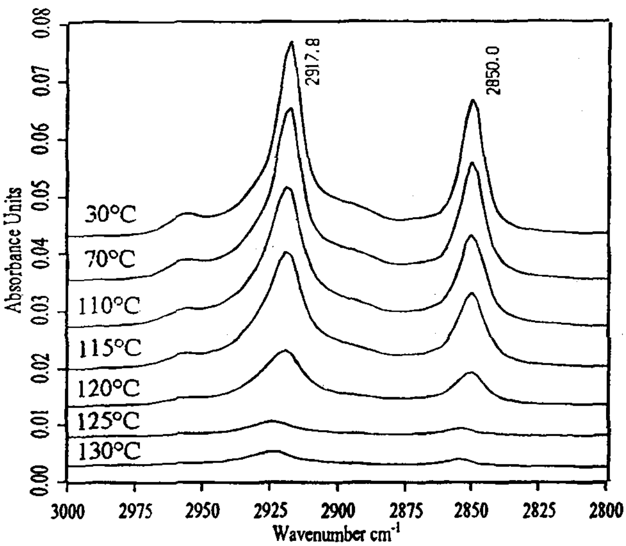


FIG. 3. Variable temperature FTIR spectra in the 3000–2800 cm^{-1} region of 11-monolayer the *N*-octadecanoyl-L-alanine LB film.

alkyl chains[11] and the decrease of intensity was attributed to the loose packing of the hydrocarbon chains and increased disorder of chain conformations.[12] The temperature-dependent frequency change of the $\nu_a(CH_2)$ band, together with the bandwidth and integrated intensity changes against temperature are plotted in FIG. 4, the temperature corresponding to the middle point between highest and lowest values of the $\nu_a(CH_2)$ frequencies reflects the order–disorder transition temperature, approximately T_c = 122 °C. Compared with the $\nu_a(CH_2)$ frequency change, the $\nu_a(CH_2)$ integrated intensity shows a concomitant and opposite change, but the bandwidth exhibits a progressive increase with temperature. Below T_c, the alkyl chains in the film take highly ordered *all-trans* conformations, the increase in temperature gives rise to an enhanced molecular thermal motion

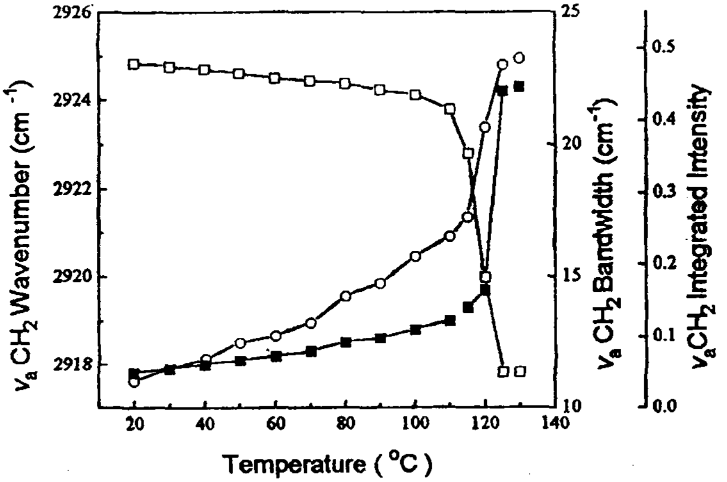


FIG. 4. Temperature dependence of the frequency(●), bandwidth (○), and integrated intensity (□) of the $v_a(CH_2)$ band in the FTIR spectra of the *N*-octadecanoyl-L-alanine LB film.

which increases the chain mobility, and the population of *gauche* conformations which decrease the density of chain packing, finally leads to the order–disorder phase transition of the film.

FIG. 5 shows the variable temperature FTIR spectra of band progression arising from the CH_2 wagging vibrations of the *trans* hydrocarbon chains. A series of absorption bands overlapped with the coupled mode of C–O stretching and O–H in-plane bending vibration appear in the spectrum of 30 °C, indicating the close packing of the hydrocarbon chains. The intensities of band progression decrease gradually with temperature resulting from the introduction of *gauche* conformations in the chains. A simple model was proposed to evaluate the contents of *gauche* conformers from the decrease of band intensity.[13] Around T_c

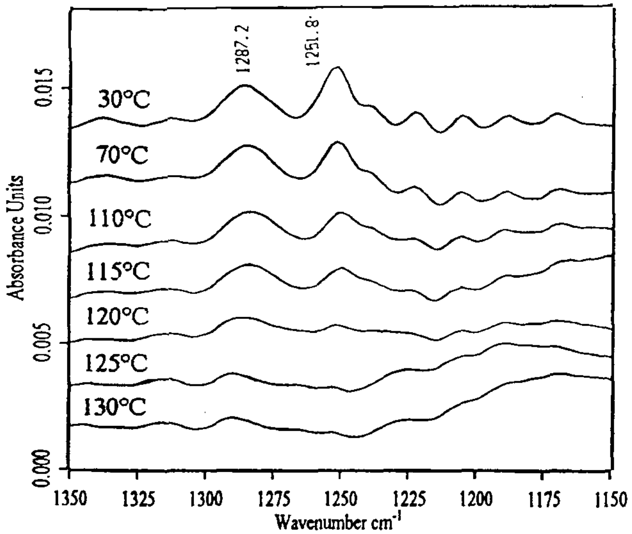


FIG. 5. Variable temperature FTIR spectra in the 1350–1150 cm^{-1} region of the *N*-octadecanoyl-L-alanine LB film.

(122 °C), the band progression nearly disappears, the increasing population of *gauche* conformers in the chains leads to the occurrence of the phase transition.

FIG. 6 shows the variable temperature FTIR spectra of the *N*-octadecanoyl-L-alanine LB film in the regions of 3400–3250 and 1600–1350 cm^{-1}. The amide A band [ν(N–H), 3324 cm^{-1}] takes a downshift to 3332 cm^{-1}, and the amide II band [δ(N–H), 1538 cm^{-1}] does an upshift to 1533 cm^{-1} at 120 °C, along with a gradual decrease of intensities, and above T_c, neither of both bands is discernible. These changes indicate that below T_c, the increase in temperature gives rise to a weakened hydrogen bond as well as an increased disorder of chain conformations. As seen from the amphiphilic structure of FIG. 1, the fact that the transition temperature of the *N*-octadecanoyl-L-alanine LB film (122 °C) is far higher

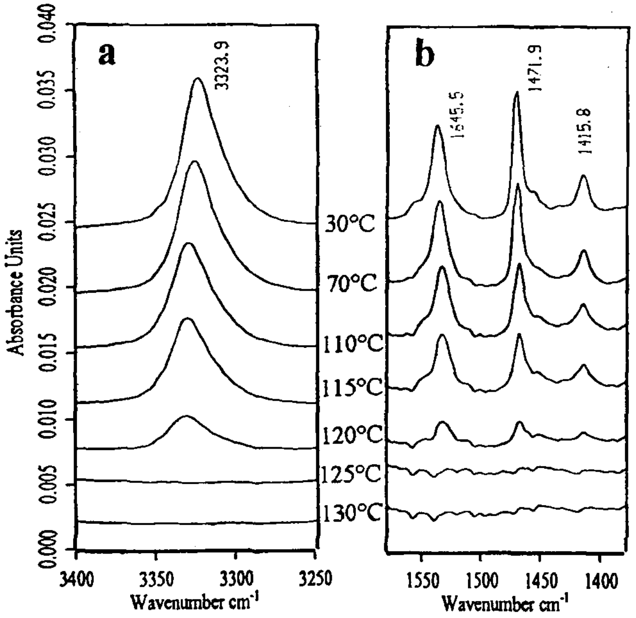


FIG. 6 Variable temperature FTIR spectra of the *N*-octadecanoyl-L-alanine LB film in the regions of, (a) 3400–3250, and (b) 1600–1350 cm^{-1}.

than that of the same-chain-length stearic acid LB film (65 °C)[14] originating from the chiral effect of enantiomers[1] and the hydrogen-bonding interactions between the hydrophilic headgroups. The hydrogen-bonding interactions between the headgroups enhances the interactions between the hydrophobic alkyl chains accordingly. In FIG. 6 (b), the 1472-cm^{-1} singlet at 30 °C, indicative of a triclinic subcell chain packing,[3] shifts down to 1468 cm^{-1} at 120 °C along with the decreased intensity and broadened bandwidth, and finally disappears above T_c (122 °C). These changes indicate the chain packing is transformed from the triclinic subcell to a hexagonal subcell, then to a liquid-like phase. However, the frequency of the $C_\alpha H_2$ and $C_\alpha H$ bending modes nearly remains unchanged (around 1415 cm^{-1}) with temperature besides the reduced intensity.

3. 3 Variable Temperature FTIR of Zinc Octadecanoyl-L-alaninate LB Film

FIG. 7 shows the temperature-dependent FTIR spectra of a 11-monolayer zinc octadecanoyl-L-alaninate LB film in the various regions of (a) 3400–3200, (b) 3000–2800, (c) 1600–1500, and (d) 1500–1425 cm^{-1}. The intermolecular hydrogen-bonding interaction in the zinc salt is enhanced as compared to that in the acid form. In FIG. 7 (a), the ν(N–H) frequency shifts gradually to a higher wavenumber together with a diminished intensity, which indicates that the intermolecular hydrogen bonds dissociate progressively with temperature. At the same time, the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ stretching bands also exhibit similar changes to the ν(N–H) band; below 110 °C, the magnitude of the increase in $\nu(CH_2)$ frequencies is little, and above it, the band frequencies increase gradually with temperature. From the discussion in Section *3. 2*, the hydrogen-bonding interactions between the headgroups simultaneously enhance the interchain interaction. The relatively strong hydrogen-bonding interaction in the zinc salt LB film is weakening with temperature, and the $\nu(CH_2)$ frequencies take a comparably gradual increase.

In FIG. 7 (c) and (d), the ν_a(COO) and ν_s(COO) band intensities decrease with temperature, however the corresponding frequencies remain constant at 1556 and 1458 cm^{-1}. No significant temperature dependence on the ν_a(COO) band frequencies below the melting point was observed for metal salts of some fatty acids.[15] In FIG. 7 (d), the $\delta(CH_2)$ frequency gradually shifts to a lower wavenumber from 1468 cm^{-1} along with a decreased intensity so that the band is submerged by the ν_s(COO) band. This change process indicates that the chain packing is transformed from hexagonal subcell structure to a liquid-like state.

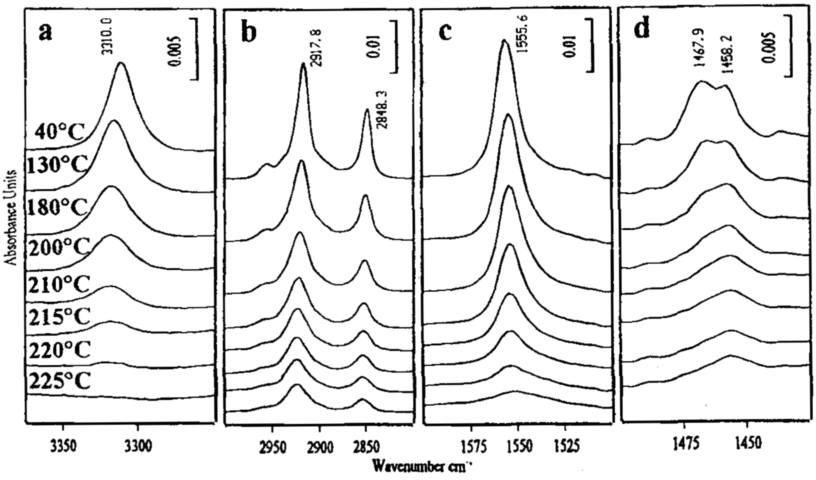


FIG. 7. Variable temperature FTIR spectra of the 11-monolayer zinc octadecanoyl-L-alaninate LB film in the regions of, (a) 3400–3200, (b) 3000–2800, (c) 1600–1500, and (d) 1500–1425 cm^{-1}.

To gain an insight into the difference in the phase behaviors of the *N*-octadecanoyl-L-alanine and zinc octadecanoyl-L-alaninate LB films, FIG. 8 shows the $\nu_a(CH_2)$ and $\nu(N–H)$ frequency changes of the two films against temperature together with the $\nu_a(CH_2)$ frequency change of the stearic acid LB film previously reported[14] for comparison. As seen from FIG. 8, there are abrupt increases of $\nu_a(CH_2)$ frequencies (curves a and e) in the both *N*-octadecanoyl-L-alanine and stearic acid LB films around their respective transition temperatures, and the similar phase behaviors take place for the two films. But below the respective transition temperatures, the $\nu_a(CH_2)$ frequency of the stearic acid film (e) keeps unchanged with temperature, which indicates the characteristics of the interchain interaction. In the *N*-octadecanoyl-L-alanine film, the intermolecular hydrogen-bonding interactions between the headgroups enhance the interactions between

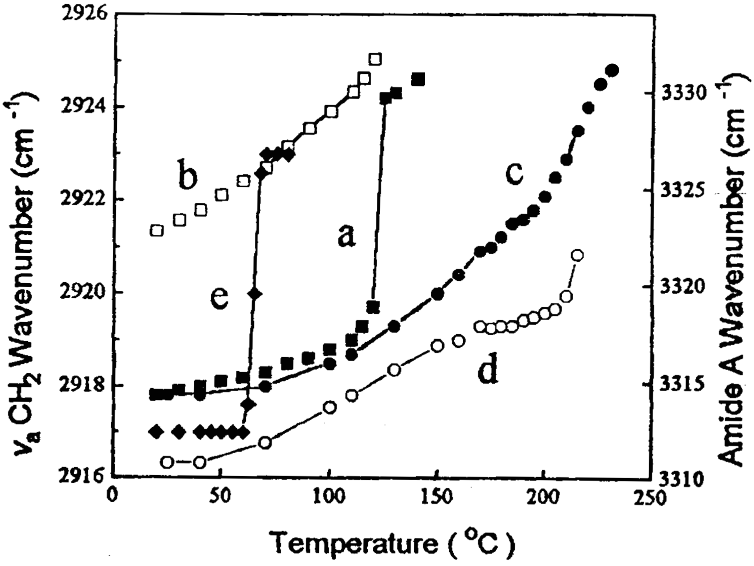


FIG. 8. Temperature dependence of the frequencies of, $\nu_a(CH_2)$ (■, a), and ν(N–H) (□, b) in the *N*-octadecanoyl-L-alanine LB film; $\nu_a(CH_2)$ (●, c), and ν(N–H) (○, d) in the zinc octadecanoyl-L-alaninate LB film; and $\nu_a(CH_2)$ (◆, e) in the stearic acid LB film from ref 14.

the alkyl chains; heating results in a gradual dissociation of hydrogen bond (b) together with a weakening interchain interaction, thus the $\nu_a(CH_2)$ frequency takes a slow increase trend (a), and around the transition temperature, the hydrogen-bonding interaction is almost disrupted and a remarkable change in $\nu_a(CH_2)$ frequency (a) is observed. The transition temperature of the *N*-octadecanoyl-L-alanine LB film (122 °C) is far higher than that of the stearic acid LB film (65 °C),[14] which is because the extended hydrogen-bonding interaction between the enantiomeric headgroups results in an enhanced interaction between the alkyl chains.

But in the zinc octadecanoyl-L-alaninate LB film, the intermolecular hydrogen-bonding interaction is further intensified, the interchain interaction induced by the hydrogen bond thus plays a dominant role in determining the phase behavior of the film. The intensified hydrogen bond takes a stepwise dissociation over a wide temperature range (d), and the corresponding $\nu_a(CH_2)$ frequency displays a monotonic increase (c) with temperature, leading to the occurrence of a different phase behavior. As a consequence, the intermolecular hydrogen-bonding interaction can not only increase transition temperature and improve film stability, but also alter phase behavior in case of an intensified interaction.

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