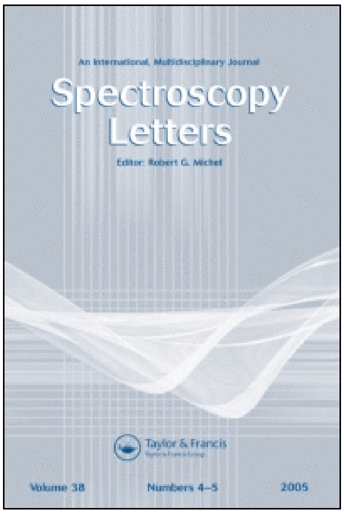

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FTIR STUDIES ON LB FILM OF AMPHIPHILE WITH SCHIFF BASE AS HEADGROUP AND ITS COPPER COMPLEX

KEY WORDS: Schiff base, LB film, Fourier transform infrared spectroscopy, Molecular orientation, Order-disorder transition

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ABSTRACT

Two different ways to form monolayers and LB films (surface film and subphase film) of the complex have been used, where a novel amphiphile containing Schiff base as a headgroup was used

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as a ligand. The monolayer behavior at the air/water interface was characterized by π–A isotherms and two-dimensional molecular orientation of alkyl chains in LB films and thermal stability were measured by polarized and variable temperature FTIR transmission spectra, indicating that the LB film of the novel amphiphile and its copper(II) complex are very stable as well as stearic acid. Because incorporating the metal ion into the monolayer makes it more condensed, thermal stability of the LB film was enhanced. As can be compared from their structure and properties, subphase films are superior to surface films.

INTRODUCTION

Functional complexes have optical, electrical, thermal, and magnetic properties, which can be enhanced owing to order aggregation in LB film. They are of potential benefit to applications such as sensors, for chemical modification of electrodes, in catalytic systems, and in microelectronic devices.[1,2] In previous studies, most complexes assembled into LB films used pyridines, porphyrines and phthalocyanines as ligands. Owing to the Schiff base physiological and pharmacodynamics properties [3,4], and some of its cobalt complexes used as oxygen carriers,[5] LB films complexed with Schiff base as the ligand should have extensive applications. In previous work, Schiff base was used as a rigid segment in alkyl chains of amphiphile in order to enhance the ultimate ordering in the built-up of multilayer films.[6]

In the present papers, the novel amphiphile 2,4–dihydroxy–N–octadecylbenlizydeneamine was used as the ligand, and LB film of its copper(II) complex was prepared in two different ways. FTIR spectroscopy was mainly used to investigate the two–dimensional structure and its basic physical property in LB film, in the transition from condensed solid to liquid crystal, suggesting the thermal stabilities the complexed LB films are much better than that of the ligand.

EXPERIMENTAL SECTION

1. Compounds

1.1 Synthesis of 2,4-Dihydroxy-N-Octadecylbenzylideneamine (abbreviated as SBC_{18} hereafter)

2.6 g (0.01 mol) Octadecylamino was dissolved in 50 mL absolute ethanol and then 1.4 g (0.04 mol) 2,4-dihydroxybenzaldehyde in 20 mL of absolute ethanol was added into the solution. The mixture was heated to the boiling point and kept boiling for 2 hr, at this time an orange solution was obtained. The solution was cooled to room temperature, placed in a freezer for 12 hr, and the yellow solid formed was filtered off. After dissolving the solid in hot ethanol and filtering, 50 mL of doubly distilled water was added into the filtrate, where an orange solid

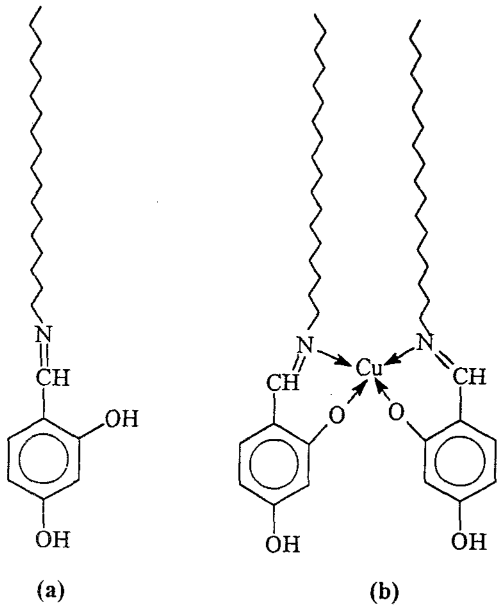


Fig. 1. Chemical structure of SBC_{18} (a) and $Cu(SBC_{18})_2$ (b).

powder was obtained. The process was repeated several times and the powder was dried in a vacuum desiccator at room temperature, this powder represents the pure product. Yield 3.1 g, 79.1%. IR (Bruker RFS 66V, KBr disk, cm^{-1}): 3412.2 (ν_{OH}), 2957.0 (ν_{CH3}), 2920.1 (ν_{CH2}), 2850.4 (ν_{CH2}), 1645.4 ($\nu_{C=N}$), 1601-1534.2 ($\nu_{benzene}$); ^{1}HNMR (Bruker 500 MHz, $CDCl_3$) δ: 8.43 (1H, CH=N), 6.95-7.05 (3H, benzene), 1.38 (2H, C-CH_2-C), 0.864(3H, C-CH_3). The chemical structure of SBC_{18} is shown in Fig. 1a.

1.2 Synthesis of Bis(2,4-dihydroxy-N-octadecylbenzylidene-aminato) copper(II) (abbreviated as $Cu(SBC_{18})_2$ hereafter)

1.8 g SBC_{18} (0.01 mol) was dissolved in 50 mL boiling absolute ethanol, a solution of 0.5 g of copper(II) acetate was dissolved in 30 mL absolute ethanol and was added dropwise to the boiling solution through filtration over 5 min. When the solution is kept boiling and refluxing for at least 12 hours, a brown solution could then be obtained. After placing the solution in a freezer for a week, the brown solid was then filtered and dried in a vacuum desiccator at room temperature. The powder was recrystallized several times from hot ethanol, resulting in a pure brown solid. ESA- MS: m/z =418.7; calculated: m/z = 417.8. The chemical structure of $Cu(SBC_{18})_2$ is shown in Fig. 1b.

2. Measurement

The experiments for monolayer spreading and the deposition of LB films were performed on a KSV5000 Langmuir trough system (KSV Instruments, Finland). A Wihelmy plate was used as the surface pressure sensor and situated in the middle of the trough. Two barriers were compressed symmetrically at the same rate from two sides of the trough. All measurements were carried out at 25°C. Monolayers were obtained by spreading 150 μL of chloroform solution composed of the amphiphile SBC_{18}, with the concentration of 1 mM, onto pure water (pH = 6.09). The pure water was doubly distilled after deionization using a Milli-Q ion exchange resin apparatus. After spreading, 15 min was allowed for solvent evaporation, and the monolayer was compressed at the rate of 20 mm/min, then the π–A isotherm was measured, which can be repeated. When reaching preset pressure, 30 min was allowed for stabilizing pressure, and then fabricating LB films onto CaF_2 substrates by the vertical dipping method. The typical dipping rate was 2 mm/min. The CaF_2 substrates were refluxed in the chloroform solvent at least 12 hr. After the deposition of the first monolayer, the CaF_2 substrates were kept dry in air for 30 min, so that the following monolayers were successfully transferred.

FTIR transmission spectra were recorded through a Bruker IFS 66V spectrometer equipped with a DTGS detector. A ZnSe polarizer was employed for polarization measurements of LB films. All spectra were collected for 1000 co-added interferograms with a resolution 4 cm^{-1}. Ultimate spectra was obtained by subtracting spectra of corresponding blank CaF_2 substrate from spectra of substrate with LB films. For the measurement of infrared spectra at elevated temperature, the CaF_2 substrate with the deposited LB films was mounted into a heating cell. Temperature control was achieved with a P/N21.500 automatic temperature controller (Graseby Specac Inc.) through a copper–constant thermocouple with an accuracy of ±1°C. After the temperature was raised to the preset value, 15 min was allowed for the thermal equilibrium.

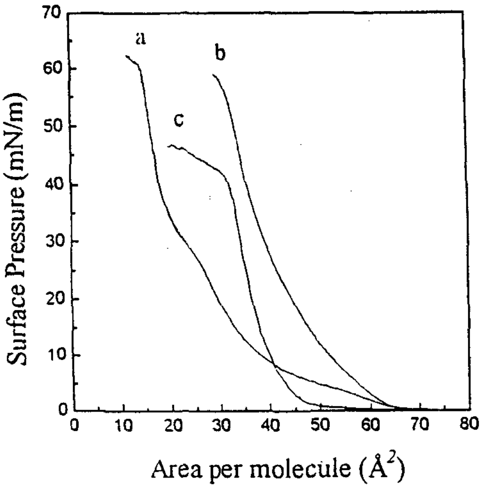


Fig. 2. π–A isotherm of (a) SBC_{18} in pure water, PH~6.09 (b) $Cu(SBC_{18})_2$ pure water, PH~6.09 (c) SBC_{18} in $Cu(AC)_2$ aqueous, PH~6.25 at 27±1°C.

RESULTS AND DISCUSSION

1. π–A isotherms of SBC_{18} and $Cu(SBC_{18})_2$

Figs. 2a and b show π–A isotherms of amphiphile SBC_{18} on pure water and $Cu(SBC_{18})_2$ on pure water (PH~6.09), respectively, while Fig. 2c shows π–A isotherm of amphiphile SBC_{18} on *1 mM* copper(II) acetate aqueous solution (PH~6.25) at 27±1°C. As can be seen from Fig. 2a, the π–A isotherm of amphiphile SBC_{18} appears as a sign of phase transition from the liquid phase to the solid phase, and the cross–Mean sectional area per SBC_{18} molecule is 27.5Å^2. Curves b and c are similar and no phase transition appears, which suggests that the π–A isotherms of the same complex have been obtained. Note that the LB film from curve b is named *surface film* and LB film from curve c is named *subphase film*. The mean cross–sectional area per $Cu(SBC_{18})_2$ molecule are 55 Å^2 and 47 Å^2 in curves b and c, which are larger than the area per ligand molecule. This is caused by a larger headgroup of the complex owing to copper(II) coordination to two ligands. Yet the π–A isotherms of amphiphile $Cu(SBC_{18})_2$ are more condensed than SBC_{18}, where curve c is the most condensed, caused by an introduction of metal ion. Incorporating metal ion into the monolayer makes it more condensed, effectively enhancing the thermal stability of the LB film[7]. This is in agreement with its higher phase transition temperature Tc, investigated by variable FTIR spectroscopy.

2. FTIR spectra of LB film

Figs. 3a, b and c show FTIR transmission spectra of a 9-monolayer LB film of SBC_{18}, a 9-monolayer surface film, and a 9-monolayer subphase film of $Cu(SBC_{18})_2$, respectively. The frequency of the free O-H stretching vibration appears in the range of 3730 ~ 3600 cm^{-1}. The hydrogen bonded O–H frequency downshifts and becomes broader; the frequency shifts to 3450 ~ 3400 cm^{-1} when intermolecular hydrogen bonds are formed, and shifts to ~ 2600 cm^{-1} when intramolecular hydrogen bonds exist.[8] As can be seen from Figs. 3a, b, and c, the broad bands at ~3446

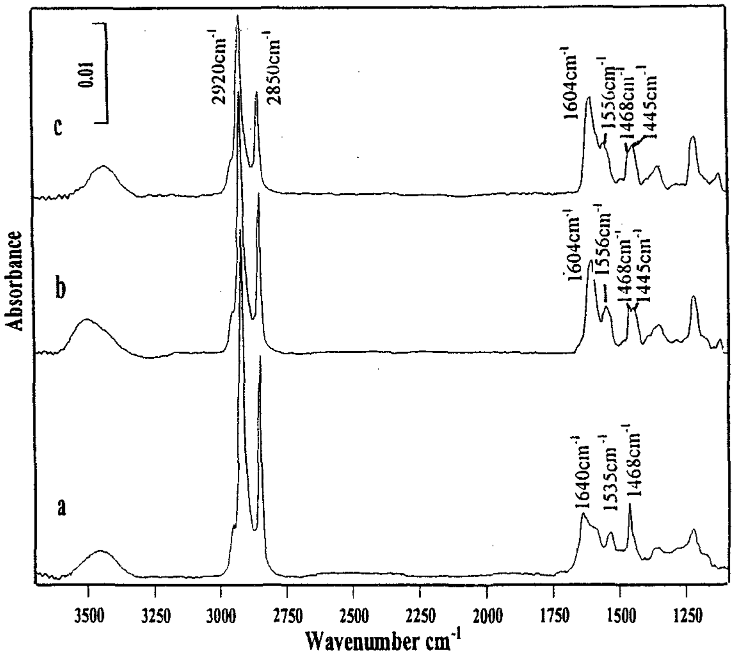


Fig. 3. FTIR transmission spectra of 9-monolayer (a) LB film of SBC_{18} (b) surface film of $Cu(SBC_{18})_2$ (c) subphase film of $Cu(SBC_{18})_2$.

cm^{-1} (3450 cm^{-1} in Fig. 3b) all appear, indicating intermolecular hydrogen bonds exist in the three kinds of LB films, which are shown in Fig. 4. The two strong, sharp bands at 2920 cm^{-1} and 2850 cm^{-1} appear, assigned to the antisymmetric and symmetric CH_2 stretching vibration mode, respectively. The frequency of the antisymmetric CH_2 stretching vibration is sensitive to the conformational order of alkyl chains. [9] The frequency at 2920 cm^{-1}

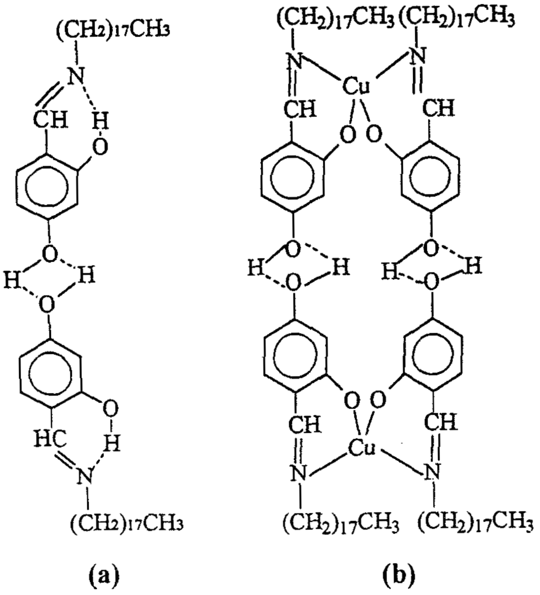


Fig. 4. Hydrogen bond formation of (a) SBC_{18} molecules (b) $Cu(SBC_{18})_2$ molecules

is characteristic of the *trans* conformation of hydrocarbon chains. In the range of 1750~1100 cm^{-1}, spectra of Figs. 3b and 3c are similar, implying the LB film of the same complex can be obtained by two different ways and they have the similar molecular structure in LB film, while they are different from Fig. 3a. The two bands at 1640 cm^{-1} and 1600 cm^{-1} overlap into a broad band in Fig. 3a, while in Figs. 3b and 3c, a strong band at 1604 cm^{-1} appears and the band at ~1640 cm^{-1} disappears, owing to metal ions coordition to ligands. This suggests the band at 1640 cm^{-1} is

TABLE 1. Band assignment of LB films of SBC_{18} and $Cu(SBC_{18})_2$ (in cm^{-1})

SBC_{18} LB film	$Cu(SBC_{18})_2$ LB film	assignment
3446	3500	O–H in intermolecular hydrogen bond
2920	2918	CH_2 antisymmetric stretching
2850	2850	CH_2 symmetric stretching
1640 1600	1602	benzene
1535	1558	C=N stretching
1468	1469	CH_2 scissor
	1445	CH_2 wagging
1375	1355	CH3 deformation
1277.6		O–H in intramolecular hydrogen bond
1226	1217	*o*-phenyl
109	1126	C–O in chelate ring

characteristic of keto-formation of Schiff base SBC_{18} including intramolecular hydrogen bond, which is in agreement with previous studies.[8] At the same time, the band at 1535 cm^{-1} in Fig. 3a, assigned to CH=N stretching vibration mode, upshifts to 1556 cm^{-1} in Figs. 3b and 3c, owing to copper(II) coordination to the ligand SBC_{18}. The CH_2 scissoring vibration mode is well known to be extremely sensitively to interchain interactions,[10] so a sharp, narrow peak at 1648 cm^{-1} is indicative of a hexagonal subcell packing as in Figs. 3a, b and c. In Figs. 3b and 3c, the two bands at 1445 cm^{-1} and 1468 cm^{-1} overlap, which is possibly caused by copper(II) coordination to SBC_{18} to form a chelate complex. Band assignments in Figs. 3a, b and c are shown in Table 1.

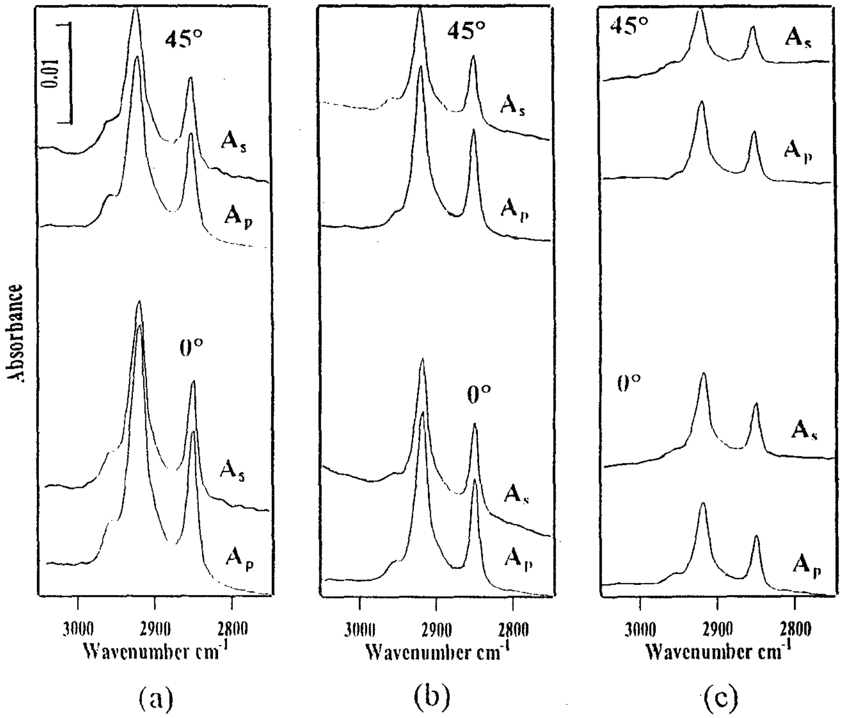


Fig. 5. Polarized FTIR transmission spectra in CH_2 stretching vibration region of (a) LB film of SBC_{18} (b) surface film of $Cu(SBC_{18})_2$ (c) subphase film of $Cu(SBC_{18})_2$.

3.Molecular orientation of LB film

Polarized FTIR spectra can be used to probe orientation of an alkyl chain. Figs. 5a, b and c show the polarized infrared transmission spectra for a 9-monolayer LB film of SBC_{18}, surface film, and subphase film of $Cu(SBC_{18})_2$ in the CH_2 stretching vibration region, whose incident angles are 0° and 45°, respectively. When the incident angle is 0°, the polarized dichroic ratios ($D=A_s/A_p$) are 1.004, 0.899 and 0.894, as in Figs. 3a, b and c. These results imply the SBC_{18} molecules take a unaxial orientation and $Cu(SBC_{18})_2$ molecules take a antisotropic biaxial orientation. This orientation, most likely indicates that coordinated parts of $Cu(SBC_{18})_2$ are forming a close-packing superlattice network that is subject to the shear forces induced during film transfer.

Molecular orientation of the alkyl chain in LB film is the main means to characterize the two-dimensional structure, and also relates to many functions, for example, the efficiency of energy transfer and the rate of photoinduced electron transfer. A Cartesian coordinate system was used to define the orientation angle of alkyl chains of LB film. The Fresnel equation and Descartes laws are as following:

$$= A_s(i=0) / A_p(i=0)$$

$$\cos 2\omega = (1-\alpha)/(1+\alpha)$$

$$n_1 \sin i = n_3 \sin r$$

$$= 2\pi d / \lambda$$

$$\beta_i = A_p(i \neq 0) / A_p(i=0) = (n_1+n_3)n_1n_3 / (n_3 \cos i + n_1 \cos r)$$

$$\{[n_1^2 \sin^2 i ctg^2 \phi / n_2^4 \cos^2 2\omega] + \cos i \cos r / n_1n_3\}$$

Where i is the incident angle, r is the refractive angle, d is the thickness of the LB film, λ is the wavelength of polarized light, the refractive index $n_1=1.0$ (in air), $n_2=1.5$ (LB film), $n_3=1.415$ (CaF_2

TABLE 2. Orientation of three kinds of LB films in solid phase

LB film	pressure	spectra	D (i=0°)	$\frac{Ap(i=45^\circ)}{Ap(i=0^\circ)}$	orientation of transitional moment	orientation of hydrocarbon chain
SBC_{18} LB film	45mN/m	$\nu_{as}(CH_2)$	1.006	0.846	68.7°	30.3°
		$\nu_s(CH_2)$		0.842	69.6°	
$Cu(SBC_{18})$ surface film	30mN/m	$\nu_{as}(CH_2)$	0.899	0.826	73.9°	23.7°
		$\nu_s(CH_2)$		0.829	73.1°	
$Cu(SBC_{18})$ subphase film	30mN/m	$\nu_{as}(CH_2)$	0.894	0.820	74.1°	22.1°
		$\nu_s(CH_2)$		0.819	75.3°	

substrate). From experimental polarized spectra shown in Fig. 5, $A_p(i=0)$, $A_s(i=0)$ and $A_p(i\neq0)$ can be obtained, which were put into the above equations and laws, ϕ_a and ϕ_s can be obtained, thus according to the relation:

$$\cos^2\phi_a + \cos^2\phi_s + \cos^2\gamma = 1$$

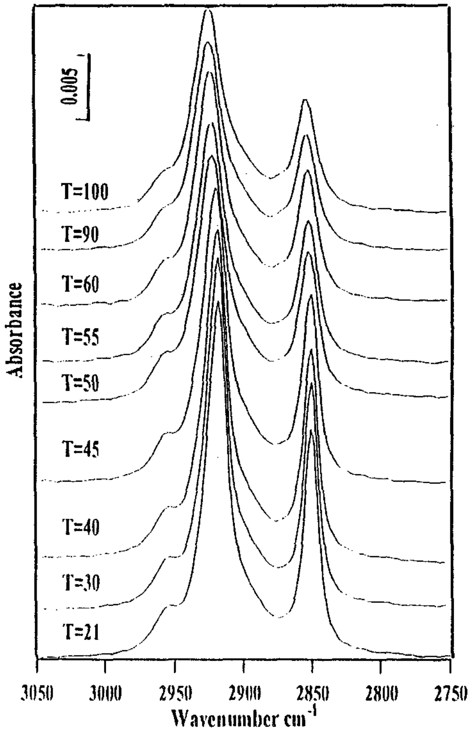
The orientation angles of the hydrocarbon chains of the three LB films can be obtained, which are shown in TABLE 2.

The orientation angle of the LB film of amphiphile SBC_{18} is similar to that of stearic acid, implying it can form stable films. The orientation angle of the alkyl chains of LB film of SBC_{18} is larger than that of surface film and the subphase film of a complex. That is, alkyl chains of a complex are closer to the surface normal, which is in agreement with a smaller orientation angle owing to the introduction of metal ion. The orientation angle of alkyl chains of subphase film is smaller than that of surface film, which is in agreement with the result that the π–A isotherm of subphase film is more condensed than that of surface film.

4. Order-Disorder transition of LB film

Figs. 6a, b and c show the FTIR transmission spectra of a 9-monolayer LB film of SBC_{18} , a surface film, and a subphase film of $Cu(SBC_{18})_2$ in the CH_2 stretching vibration region at elevated temperature. As can be seen from Fig. 6, elevating temperature leads to enhanced molecular thermal motion, conformation, orientation of alkyl chains, and altered molecular aggregation. This can be indicated from shifted frequency, decreased intensity, and band broadening; indicating that order-disorder transition takes place. Phase transition is in essence that conformation of the alkyl chain changes from *trans* to *gauche*. The two bands at ~2918 cm^{-1} and ~2850 cm^{-1} appear in condensed solid film, and at ~2924 cm^{-1} and ~2854 cm^{-1} in liquid crystal. So FTIR spectra of variable temperature is an effective tool to measure order-disorder transition temperature Tc.

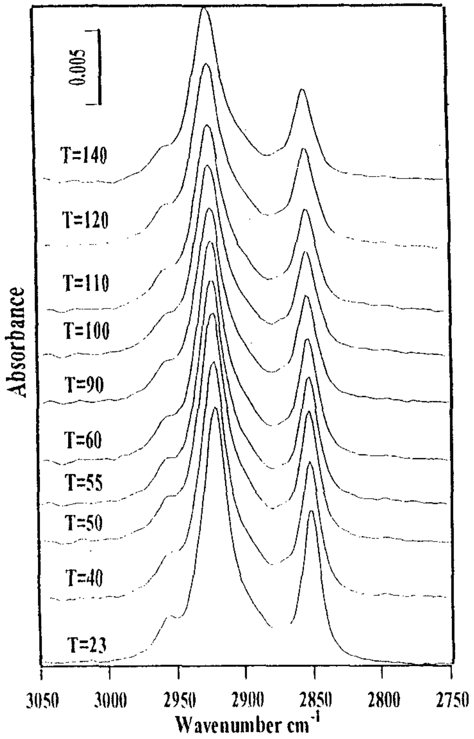
Figs. 7a, b and c plot the change of temperature-induced frequency of the antisymmetric CH_2 stretching band corresponding to Figs. 6a, b and c, respectively. At room temperature, the band is



(a)

Fig. 6. FTIR spectra in CH_2 stretching vibration region at elevated temperature (°C) of (a) LB film of SBC_{18} (b) surface film of $Cu(SBC_{18})_2$ (c) subphase film of $Cu(SBC_{18})_2$;

at 2920.5 cm^{-1}, indicating the hydrocarbon chains in the LB film primarily adopts a *trans* conformation. For LB film of SBC_{18}, the frequency changes abruptly from ~2920 cm^{-1} to ~2922 cm^{-1} in the range of 40°C ~ 60°C, then increases slowly until reaching ~2924 cm^{-1} at 100°C, which suggests the hydrocarbon chains were

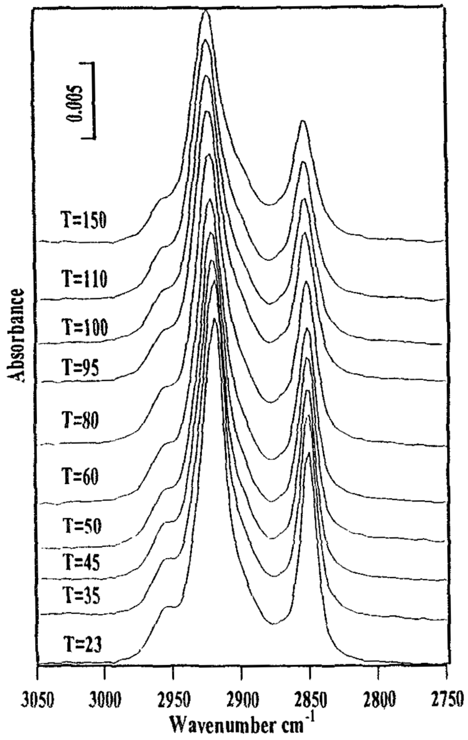


(b)

Fig. 6. Continued

(continued)

introduced to a *gauche* conformation, with phase transition temperature Tc at about 50°C. By the same method, Tc of a subphase film of $Cu(SBC_{18})_2$ is 100°C, whose frequency changes suddenly in the range of 80°C~120°C. For surface film of $Cu(SBC_{18})_2$, there are two abrupt changes at elevated temperature,



(c)

Fig. 6. Continued

one of which is in the region of 40°C~60°C and the other is 100°C~130°C. The observations suggest Tc of LB film of complex is higher than that of ligand, indicating thermal stability of LB film of complex is better and surface films of complex exhibit different phase transition behavior from subphase films of complex. The π–A isotherm of subphase complex exhibits more condensed and

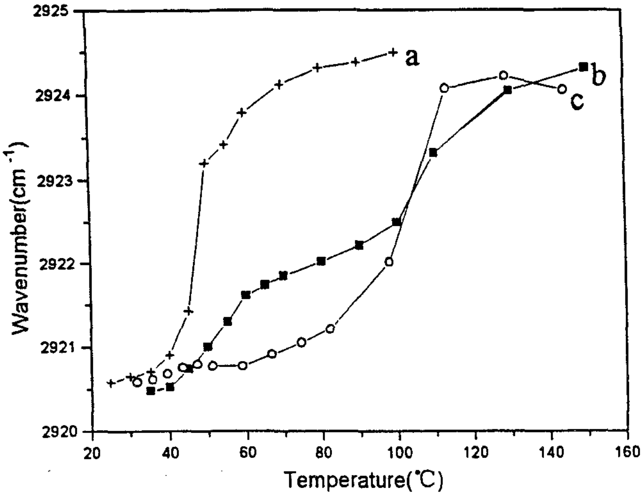


Fig. 7. Temperature dependence of wavenumber of antisymmetric CH_2 stretching bands in (a) LB film of SBC_{18} (b) surface film of $Cu(SBC_{18})_2$ (c) subphase film of $Cu(SBC_{18})_2$.

molecular orientation of alkyl chains, thus the subphase film is smaller than that of surface film, implying that molecules of subphase film pack more densely and intermolecular interaction is stronger. For surface film, coordinated parts of $Cu(SBC_{18})_2$ can be used as a rigid or semi-rigid segment in hydrocarbon chains, resulting in two abrupt changes at elevated temperatures. When this occurs one can obtain molecules of subphase film for the complex that pack more densely, are more regular, and have better thermal stability than surface films. The method of using metal ions in the subphase to interact with amphiphile is used in order to obtain a monolayer or LB film of complex.

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