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Characterization of the melting–crystallization transition of alcohol monolayers at the air/water interface by polarization modulation infrared reflection absorption spectroscopy

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Abstract

Monolayers of 1- and 2-alcohols of varying lengths have been studied at the water surface using polarization modulation infrared reflection absorption spectroscopy. At the melting of the monolayer, we observe for all compounds a sudden increase of the conformational defects. In the liquid phase the alkyl chains contain gauche defects whereas they are all-trans in the solid phase. In addition, the chains are vertical or tilted by a few degrees with respect to the normal to the surface and the anchorage of molecules at the water surface is ensured by hydrogen bonding. © 1998 Elsevier Science B.V.

1. Introduction

The study of Langmuir monolayers has been greatly developed with the introduction of many techniques such as Π–A isotherms, X-ray and neutron diffraction or Brewster angle microscopy [1,2]. However, in many cases, the data obtained need to be complemented with direct molecular information provided by vibrational spectroscopies. During the last decade, considerable efforts have been made to enhance the monolayer sensitivity of these methods [3,4]. Recently a differential IR reflectivity technique polarization modulation infrared reflection absorption spectroscopy (PM–IRRAS) has proved to be an efficient tool in obtaining orientational and conformational information at the molecular level [5,6].

We have previously been interested in characterizing the melting–crystallization transition of monolayers of short 1-alcohols (OH group on the first carbon atom of the chain) [7,8] and then in determining the influence of the polar OH head on the 2D organization. This leads us to study short molecules in order to reduce chain–chain interactions and to compare results with other alcohols in which the OH group is located elsewhere in the chain. We have thus begun to investigate monolayers of 2-alcohols (OH group on the second carbon atom of the chain) which are chiral molecules [9]. As the chiral heads are confined in a two-dimensional (2D) space the influence of the chiral part of molecules would probably be enhanced. Arnett et al. investigated confined chiral molecules [10], and in recent years the effects

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of chirality in Langmuir monolayers have been extensively studied to obtain insight into certain biological mechanisms [11–13]. It would be possible to detect an effect of the chirality on the 2D organization of 2-alcohols.

This Letter describes a PM–IRRAS study of the melting–crystallization transition of alcohol monolayers of varying length spread on the water surface. 1- and 2-alcohols were investigated and results compared. Some important results have already been obtained on these systems using X-ray diffraction and ellipsometry and can be summarized as follows [7–9]: (1) the first-order feature of the transition becomes less and less pronounced as the chain length decreases; (2) monolayers crystallize in a hexagonal rotator II phase; and (3) a strong effect of parity on the melting temperature of the drop implies that for even 2-alcohols the solid monolayer is in equilibrium with a solid drop when it is in equilibrium with a liquid drop in the case of 1- and odd 2-alcohols. The comparison between these two kinds of alcohol can give information about the influence of the polar head on the 2D organization.

2. Experimental apparatus

The optical apparatus and signal analysis of PM–IRRAS have been described in detail elsewhere [5,6].

PM–IRRAS measurements were carried out both on a home-made and on a commercial NIMA trough regulated by a circulating water system. A plastic cover with two BaF_2 windows for the IR beam transmission prevents dust contamination and water evaporation.

The subphase was milli-Q (Millipore) ultra-pure water with a resistivity higher than 18 MΩ cm. The surface pressure was measured by the Wilhelmy method using a paper filter.

1-alcohols and racemic compounds of 2-alcohols were obtained from Aldrich SA or Lancaster and used without further refinement. Pure enantiomers were synthesized by copper-catalyzed Grignard methyl oxirane opening [14]. In what follows the notation 1-C12 or 2-C12 (for 1- or 2-dodecanol) corresponds to 1- and 2-alcohol racemic mixtures respectively and the left and right enantiomers are respectively noted (L)C12 or (D)C12. We studied monolayers of (L)C12, (D)C13, (D)C14 and the corresponding racemic mixtures.

To obtain a monolayer, we deposit a drop of alcohol at the water surface: the monolayer spreads spontaneously and stays in equilibrium with the excess drop which plays the role of reservoir and compensates for any loss of matter (evaporation, dissolution, etc.) [7]. This technique allows the study of short-chain molecules for which the classical apparatus with a movable barrier is no longer applicable. The temperature is the controlling parameter in generating melting–crystallization transitions.

3. Results

For all experiments, the monolayer was formed at the water surface at a temperature above its melting temperature T_{m2D}. Successive PM–IRRAS spectra were recorded at different stabilized temperatures going from the liquid to the solid phase. Fig. 1 shows the evolution with temperature of the spectrum of a 1-C13 ($T_{m2D} = 48°C$) monolayer in the 3000–2800 cm^{-1} spectral range. These spectra display two absorption bands at 2920 and 2850 cm^{-1}, corresponding to the antisymmetric $\nu_a(CH_2)$ and the symmetric $\nu_s(CH_2)$ (Fig. 1) stretching vibrations, respectively.

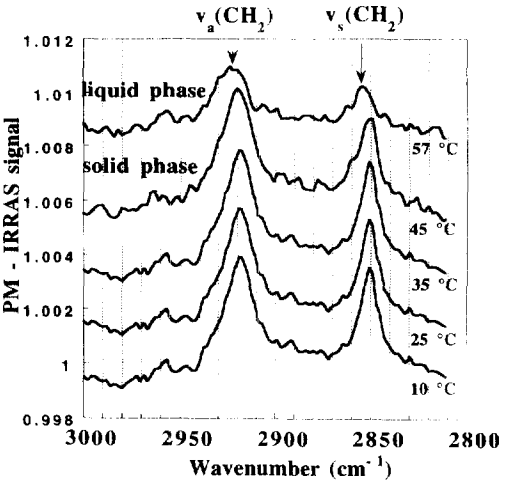

Fig. 1. PM–IRRAS spectra of a 1-C13 monolayer at different temperatures above and below the melting–crystallization transition ($T_{m2D} = 48°C$).

3.1. 1-alcohols

For all 1-alcohols (1-C10 to 1-C16), a sudden shift of the $\nu_s(CH_2)$ and $\nu_a(CH_2)$ to lower wavenumbers is observed at the crystallization of the monolayer. A correlated decrease in the full width at half maximum (FWHM) is also observed (at $T = 57°C$, bands are narrow and the Lorentzian fit is poorly defined, which introduces a strong uncertainty on the FWHM). These behaviors, shown in Fig. 2 for the 1-C13 monolayer, indicate that the molecules exhibit fewer gauche conformational defects in the solid phase than in the liquid. This fact has already been observed by Bain for 1-C11 monolayers using sum frequency vibrational spectroscopy [15]. However, the discrepancy of molecular order is less marked for the monolayers than for the corresponding bulk: for the monolayer the shifts of the $\nu_s(CH_2)$ and $\nu_a(CH_2)$ bands at the transition are lower than for the bulk (Table 1; Fig. 3). Moreover, we observe that the positions of the CH_2 modes in the liquid phase of the bulk and of the monolayer roughly coincide, while they significantly differ in the solid phase. This result is consistent with entropy measurements [16] which show that the 2D solid phase has more entropy than the 3D solid phase because of the rotation of molecules around their axis in the monolayer, whereas the 2D and 3D liquid phases have similar entropy values.

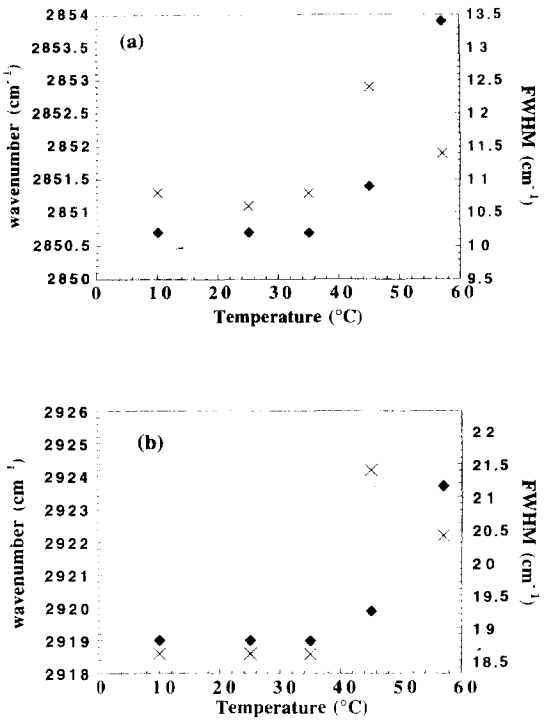

Fig. 2. (a) CH_2 symmetric stretching frequency (◆) and full width at half maximum (×) of the corresponding absorption band as a function of temperature for 1-C13; (b) CH_2 antisymmetric stretching frequency (◆) and full width at half maximum (×) of the corresponding absorption band as a function of temperature for 1-C13.

Table 1
Frequency positions of $\nu_a(CH_2)$ and $\nu_s(CH_2)$ for bulk and monolayer for 1-C14

	Bulk		Monolayer	
	$\nu_a(CH_2)$ (cm^{-1})	$\nu_s(CH_2)$ (cm^{-1})	$\nu_a(CH_2)$ (cm^{-1})	$\nu_s(CH_2)$ (cm^{-1})
Liquid	2923.5	2853.4	2923.7	2853.9
Solid	2917.0	2848.8	2919.0	2850.7
Shift	6.5	4.6	4.7	3.2

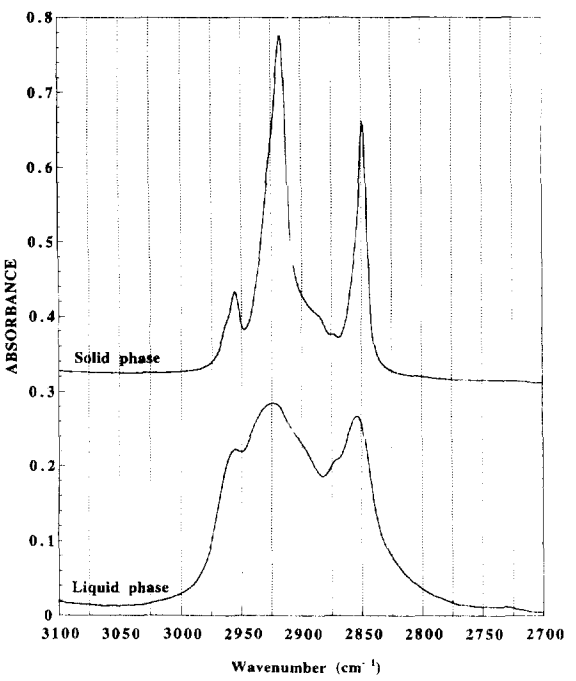

Fig. 3. Bulk absorbance spectrum of 1-C13 in the solid and liquid phases.

PM–IRRAS spectroscopy is a good tool for studying molecular orientations in ultrathin films deposited on dielectric substrates, and in particular at the water surface. Indeed the sense of an absorption band relative to the baseline and its intensity are governed by a surface selection rule depending on the average orientation of the corresponding transition moment [6]. A transition moment lying in the surface plane gives rise to an absorption band oriented positively and a transition moment perpendicular to the surface gives rise to a absorption band oriented negatively, with respect to the baseline. Between these two extreme cases a general orientation of the transition moment leads to competitive positive and negative contributions. For a particular 'vanishing' angle α, with a value which depends on the refractive index of the substrate [6], the two contributions balance and thus the absorption band is not observable.

To determine the orientation of the aliphatic chain molecules, we studied the CO stretching mode whose absorption band is located at 1060 cm^{-1}. We know that the OH polar group at the extremity of the chain points into the water [17]. Thus if the chain is all-trans, the orientation of the CO band gives the tilt of the chain axis with respect to the vertical. At 1060 cm^{-1} the refractive index of water is $n = 1.24$ which corresponds to a vanishing angle $\alpha = 37°$. For all 1-alcohol monolayers, the PM–IRRAS intensity of the CO absorption band is either zero or very slightly negative when its corresponding bulk ATR intensity is strong, as illustrated in Fig. 4a in the case of 1-C14. This indicates that the CO bond is tilted by slightly less than 37° from the normal to the surface. Moreover, considering the sp^3 tetrahedral hybridization of the carbon and oxygen atoms, we expect an angle $\alpha_v = 35.5 \pm 0.5°$ between the CO bond and the chain axis. This shows that the aliphatic chains are perpendicular to the surface within the accuracy of the experiments. This result is supported by the strong CH_2 absorption bands on the monolayer spectrum (Fig. 4b) which imply that the corresponding transition moments lie in the surface plane.

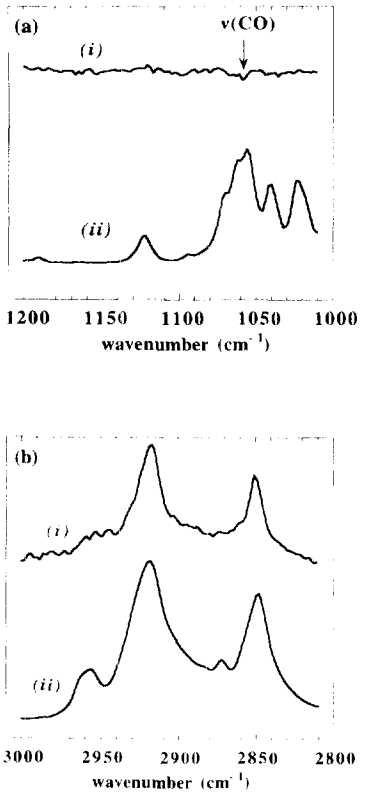

Fig. 4. Monolayer PM–IRRAS (i) and bulk absorbance (ii) spectra of 1-C14.

3.2. 2-alcohols

At the crystallization of the monolayer we observe the same phenomenon as for 1-alcohols: the frequency positions of the CH_2 absorption bands shift by ~ 3 cm^{-1} towards lower wavenumbers, indicating an increase of order in the alkyl chains. However, differences between 1- and even 2-alcohols appear a few degrees below T_{m2D}. Fig. 5 shows the frequency position and the integrated intensity of the $\nu_s(CH_2)$ band of 2-C12 ($T_{m2D} = 9°C$ and $T_{m3D} = 7°C$) as a function of time as the temperature slowly decreases to 3°C (the rate of decrease is $\sim 7°C/h$). When the monolayer crystallizes ($t \approx 40$ min), we observe the frequency shift and an increase of the integrated intensity: the number of defects decreases. In the case of even 2-alcohols, the crystallization temperature of the drop is close to that of the monolayer whereas it is significantly lower for 1- and odd 2-alcohols. In Fig. 5 the transition observed at $t \approx 130$ min corresponds to the crystallization of the drop. At this time, the number of gauche defects in the monolayer suddenly increases to reach values

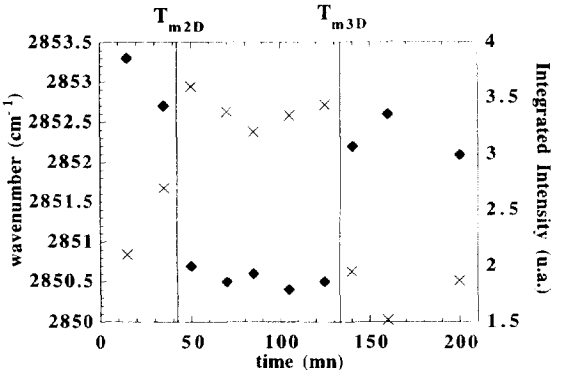

Fig. 5. CH_2 symmetric frequency (◆) and integrated intensity (×) of the corresponding absorption band as a function of time for 2-C12 during a decrease of temperature. Times corresponding to the 2D and 3D melting–crystallization transitions are also indicated.

that differ little from those encountered in the liquid phase, as indicated by the $\nu_s(CH_2)$ frequency position. In the same time the integrated intensity decreases, indicating that the number of molecules per unit area has decreased. It is possible that when the drop is solid, the loss of matter at the surface is no longer compensated. This explanation is supported by the fact that a sudden decrease of the surface pressure is observed when the reservoir drop crystallizes [9]. Molecules are less constrained and gauche defects can be formed more easily. The same phenomenon occurs in the monolayer of the pure enantiomer (D)C12.

To understand the anchorage of the 2-alcohols at the water surface, we studied the PM–IRRAS spectra of monolayers in the CO and OH stretching domains. The absorption band of the CO mode is not detectable for all 2-alcohols studied, either racemic or enantiomers. This indicates that the CO bond is tilted by $\sim 37°$ from the normal to the surface. More information can be drawn from the ν(OH) spectral domain. Indeed, we observe a very weak negative band located at ~ 3300 cm^{-1}. It is known that formation of hydrogen bonds influences the covalent bond and induces a shift of the absorption band from 3500 to 3300 cm^{-1}. These observations indicate the formation of hydrogen bonds between the polar heads of alcohol molecules and the water molecules of the subphase. Indeed, if hydrogen bonding were present between alcohol molecules, the ν(OH) transition moment would lie quite parallel to the interface resulting in a positive and rather intense band on the PM–IRRAS spectrum.

4. Conclusions

The very high sensitivity of PM–IRRAS allows molecular information to be obtained on the melting–crystallization transition of alcohol monolayers at the air/water interface. This transition results in a dramatic increase of the number of gauche defects in the aliphatic chains. In the solid phase of monolayers, molecules are quite perpendicular to the interface, and the anchorage of the polar head is ensured by hydrogen bonds with the water molecules of the subphase. In the case of 2-alcohols our results are consistent with the chains being no more tilted than 1-alcohols and with the presence of a conformational defect on the C2–C3 bond to point the OH group toward water. We observe the same behavior for monolayers of racemic mixtures and pure enantiomers: left and right molecules adopt the same conformation whatever their neighbours. This technique does not give information on the relative orientation between molecules but we have performed other studies using methods which consider the packing of molecules.

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