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Thermodynamics of Phase Transitions in Langmuir Monolayers Observed by Vibrational Sum Frequency Spectroscopy

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Our current understanding of the physical chemistry of Langmuir monolayers remains incomplete despite significant research on these systems that dates back to the beginning of the 20th century.[1−7] While the unique geometry of the air/water interface has allowed for measurements of some macroscopic properties of these systems (e.g., pressure−area (Π-a) isotherms), the inherent experimental difficulties in garnering interfacial data has limited spectroscopic studies. This has left holes in our knowledge of certain properties of these films. For example, although it is widely accepted that gauche defects are eliminated with increased lateral pressure during the transition from the two-dimensional liquid to solid phase, no thermodynamic values have yet been reported concerning their removal.

Vibrational sum frequency spectroscopy (VSFS) has a unique ability to acquire in situ vibrational spectra from a Langmuir monolayer at the air/water interface.[8−11] The information gleaned about gauche defects and other spectroscopically observable features has, however, usually been qualitative in nature. The present study demonstrates the first acquisition of quantitative thermodynamic data for the phase transition enthalpy. This is accomplished by employing VSFS to monitor gauche defects in the monolayer and invoking the two-dimensional form of the Clapeyron equation (eq 1):

$$\frac{\mathrm{d}\Pi}{\mathrm{d}T} = \frac{\Delta S_{\mathrm{trans}}}{\Delta a_{\mathrm{trans}}} \tag{1}$$

to extract the entropy and subsequently the enthalpy changes. Here $\Delta a_{\mathrm{trans}}$ and Π, stand for area change and surface pressure, respectively. These quantities replace $\Delta V_{\mathrm{trans}}$ and P used in the standard three-dimensional case. $\Delta S_{\mathrm{trans}}$ and T represent the entropy change and temperature as usual.

Monolayer films where the alkyl chains are in an all-trans configuration have a distinct VSFS response as a result of the in-plane symmetry of the methylene groups.[12] This symmetry makes the methylene modes sum frequency inactive in the dipole approximation and as a result, spectra from such systems predominantly show evidence for methyl features. The introduction of gauche defects into the monolayer, however, breaks this symmetry, making the methylene modes sum frequency active.

Herein, VSFS was employed to observe octadecylamine (ODA) monolayers spread on acidic salt solutions[13] as a function of temperature at several fixed pressures. ODA was chosen because the monolayer remains homogeneous throughout the pressure and temperature region investigated (at least down to the diffraction limit as determined by fluorescence microscopy). As with previous VSFS studies of Langmuir monolayers,[14−16] distinct transitions between ordered and disordered states were observed as the temperature and pressure of the monolayer were altered. For example, seven spectra were obtained for an ODA monolayer as a function of temperature at a surface pressure of 14 mN/m. Three of these are shown in Figure 1a representing data just below, near, and just above the phase-transition temperature.

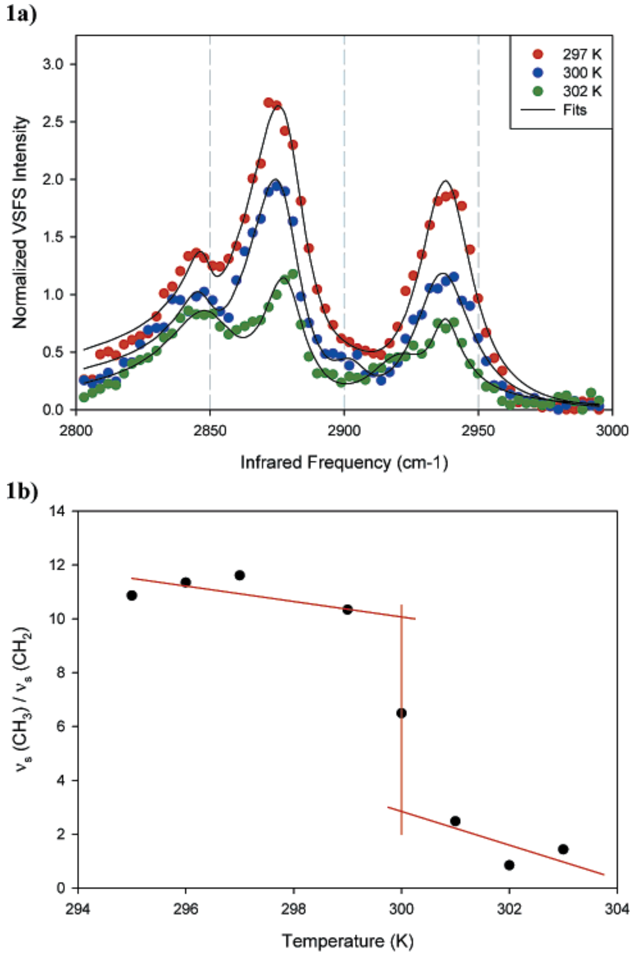

Figure 1. (a) Three VSFS spectra in the CH stretch region from an ODA monolayer spread at the liquid/vapor interface are shown. The subphase was prepared by dissolving 10 mM NaCl into D_2O and then adjusting the pH to 2.4 by the addition of HI. The monolayer was held at a pressure of 14 mN/m, while the temperature was changed. The spectra were recorded at 297 K (red), 300 K (blue), and 302 K (green). The solid lines represent fits to the data using a Lorentzian model. The data were taken with the SSP polarization combination. (b) A plot of the temperature dependence of the $\nu_s(CH_2)/\nu_s(CH_2)$ ratio from seven spectra taken at 14 mN/m.

Four features are observed and can be assigned to the methylene symmetric stretch, the methylene anti-symmetric stretch, the methyl symmetric stretch, and a convolution of the methyl anti-symmetric stretch with a Fermi resonance at 2850, 2915,[17] 2880, and 2950 cm^{-1}, respectively.[12]

It is clear from Figure 1a that as the monolayer disordered at higher temperatures, the methyl-associated features decreased

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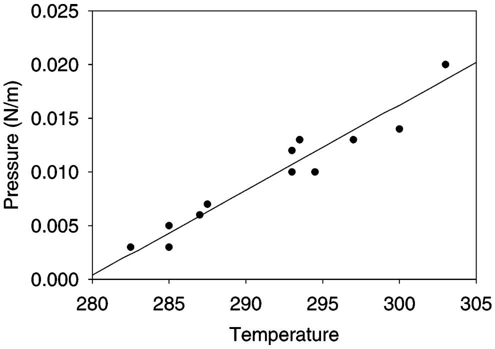

Figure 2. The Π vs T graph for the ODA monolayer's phase transitions.[19] The solid line represents a linear best fit to the data points.

significantly in intensity. This decrease can be attributed to the formation of gauche defects in the monolayer that reduced the number of methyl moieties that were well-aligned along the surface normal.[8,18] Fitting the peaks further revealed that the oscillator strength of the methylene symmetric stretch increased concomitantly with the methyl decrease. Indeed, increased methylene signal is consistent with increased formation of gauche defects at higher temperatures.

Abrupt changes in the ratio of $\nu_s(CH_3)/\nu_s(CH_2)$ can be taken as an indicator of the phase transition due to the sensitivity of these modes to the structure of the alkyl chains (Figure 1b). A plot of surface pressure as a function of the phase transition temperature (Π vs T_{trans}) and a linear fit to the data are shown in Figure 2.

The transition entropy can be obtained from the slope of the line using eq 1. The value of Δa_{trans} associated with the solid to liquid-phase transition is already well established from Π-a diagram measurements and is ~5 Å^2/molecule.[20] The calculated entropy change of the phase transition [$\Delta S_{trans} = 23 \pm 2$ J/(mol·K)] then allows the transition enthalpy to be calculated directly as a function of temperature. The value at 292 K is $\Delta H_{trans} = 7.0 \pm 0.6$ kJ/mol and corresponds to 10 mN/m. On the other hand, raising the pressure to 20 mN/m increases ΔH_{trans} to 7.3 ± 0.7 kJ/mol and the phase transition occurs at 304 K. Finally, extrapolating down to 0 mN/m leads to $\Delta H_{trans} = 6.7 \pm 0.6$ kJ/mol at a transition temperature of 280 K.

The enthalpy changes calculated for this system are particularly interesting when compared with previously reported values for gauche defect formation in alkyl chain systems. The simplest of which is gaseous butane where gauche conformers are reported to be between 3 and 4 kJ/mol higher in energy than the anti form. Enthalpic costs of a gauche defect have also been reported for bulk lipid dispersions (6.5 kJ/mol).[21] It is almost certainly the case that the relatively high value for the ODA monolayer stems from the restricted geometry at the interface. In other words, gauche defect formation at a tightly packed air/water interface requires other alkyl chains to be forced out of the way. This cost increases as a function of the two-dimensional pressure. Significantly, the extrapolated value of the phase transition enthalpy at 0 mN/m corresponds well to the lipid dispersion measurement, where no additional pressure was applied.

It is important to consider the number of gauche defects that must exist on average per chain at the phase transition in the ODA monolayer system. Given an energy difference of 7.3 kJ/mol between the gauche and trans conformers at 20 mN/m, the probability of forming a gauche defect at 304 K can be calculated using a Boltzman distribution.[22] Approximately 5.3% of the bonds are in the gauche conformation at this phase-transition temperature. There are 17 methylene units per chain, since each alkyl chain is 18 carbons in length. This leads to 16 possible gauche conformations. If each of these were equally likely to form, then roughly 58% of the chains would contain at least one gauche defect at the phase transition. It should be noted, however, that carbon–carbon bonds near the headgroup are probably less likely to adopt a gauche conformation than those further up the chain. Therefore, this estimate probably represents an upper boundary to the actual value.

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