

The Formation of Solid Monolayers of Linear Amines Adsorbed on Graphite from the Liquid

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Solid monolayer formation by all the linear amines from C₆ to C₁₆ adsorbed from their liquids to a graphite surface is demonstrated. Shorter homologues do not show such solid monolayer formation. The behavior is interpreted in terms of the competition between the alkyl chains, which favor solid monolayer formation, and the amine group, which does not. Nonylamine (C₉) also shows evidence of a solid–solid phase transition in the monolayer prior to melting.

Introduction

The physisorption of simple alkyl molecules from liquids and solutions at the solid/liquid interface is of continuing interest both academically and industrially. The adsorbed layers formed in these circumstances are key to many phenomena such as lubrication, wetting, and colloidal stability.¹ However, these interfaces are far more inaccessible than other surfaces, such as the solid/vapor interface, and this difficulty has hampered the experimental investigation of these important systems.

Recently we, and others, have exploited a number of techniques, particularly sensitive calorimetry, in the study of such adsorbed layers.^{2–5} The tiny energy changes that arise from the phase transitions of the adsorbed layer can be measured with great accuracy allowing both the temperatures and thermodynamic quantities, e.g., enthalpy of melting, to be determined. Previously, several homologous series have been investigated in this fashion including linear alkanes, alcohols, and carboxylic acids.^{6–10} In all of these cases, the materials exhibit the formation of solid monolayers that exist at temperatures above the bulk adsorbate melting point—the adsorption of a solid monolayer from the liquid. The formation of such ordered, crystalline, solid layers is very important in understanding many aspects of interfacial behavior, particularly wetting and mixing.¹¹ For example, in lubrication a disordered layer may have a lower viscosity than a solid layer, allowing contacting layers to move easily relative to one another, although a solid layer may be more mechanically robust and more difficult to push aside than a liquid.

Adsorbed layers are extremely important in the behavior of biological materials. The elementary unit of many biological materials is the amino acid consisting of an amino group (–NH₂), a carboxylic acid group (–CO₂H), together with additional functionality depending on which amino acid is under consideration. In exploring the adsorption properties of these complex materials, we have taken the approach of considering the effects of each of the parts of these materials: namely, the acid groups and amine groups separately, prior to considering the behavior of the amino acid units as a whole. We have previously investigated carboxylic acid monolayers adsorbed from their liquids and solutions^{12,13} to the solid surface of

graphite. The acid molecules are reported to be adsorbed lying flat on the surface of graphite with the carbon backbone parallel to the graphite surface. This is different from the air/water interface where they are generally aligned normal to the plane of the interface. Importantly these adsorbed layers of acids are crystalline solids at temperatures when the bulk acid is liquid. In this work we identify similar solid monolayers for linear amines adsorbed at the solid/liquid interface.

Experimental Section

Calorimetric measurements were made on a Pyris 1 Differential Scanning Calorimeter (DSC), at the BP Institute, University of Cambridge, as described previously.² The device was calibrated with indium and heptane, and the heating/cooling rate in this work was 10 °C/min, representing a compromise of temperature precision and sensitivity (e.g., slower scanning rates give better temperature precision but weaker features). All chemicals were purchased from Aldrich, with a purity >98% and used without further purification. The graphite used was Papyex, a recompressed, exfoliated graphite, commercially available from Le Carbone with a specific surface area 31.6 m²g^{–1}, determined by nitrogen adsorption. A typical DSC sample consists of 20 mg of graphite with approximately 10 mg of the amine. All samples were annealed on the graphite at elevated temperature between the bulk melting and boiling points of the adsorbate, prior to measurement.

Because DSC is a dynamic technique the position of a feature, such as melting, may be identified as the onset of the peak rather than the peak maximum, although this strictly depends on the order of the transition under consideration. However, experimentally it is often the peak maximum that is the easier quantity to measure. For the small monolayer peaks considered here these two measurements differ by a relatively small constant amount of approximately 2 degrees. Here we quote the onset temperature unless stated otherwise.

In this work we wish to investigate the adsorption from bulk adsorbate liquids. However, it is experimentally convenient to avoid excess adsorbate. Based on previous coverage-dependent studies the high coverage limit is usually obtained after the addition of only some 5–10 adsorbed monolayers. In this work, approximately 35–40 equivalent monolayers of adsorbate has been added, an estimate based on the specific surface area of

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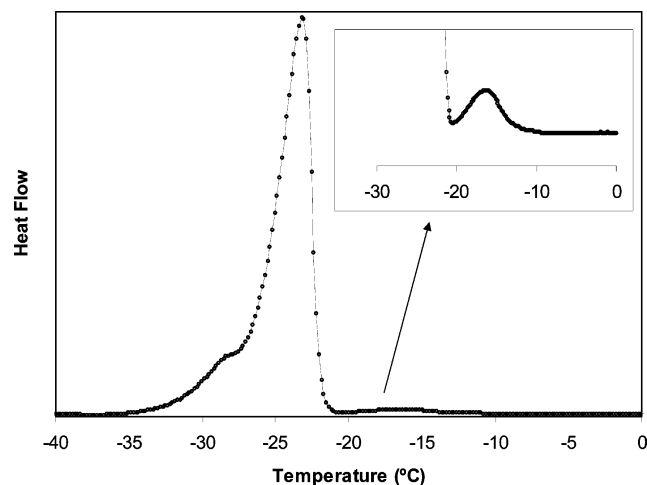


Figure 1. Thermogram from approximately 35 monolayers of heptylamine adsorbed on graphite. The large peak at approximately $-26\text{ }^{\circ}\text{C}$ is the bulk melting transition. The small peak at $-20.9\text{ }^{\circ}\text{C}$ is the monolayer melting transition. The heat flow scale of the inset is 10 times that of the main figure.

the graphite and the area per molecule. At such high coverages any small error in these estimates is negligible.

Results

Figure 1 presents a DSC thermogram for approximately 35 monolayers of heptylamine ($\text{C}_7\text{H}_{15}\text{NH}_2$) adsorbed on graphite. The very large peak with an onset at a temperature of $-26.5\text{ }^{\circ}\text{C}$ (peak at $-24\text{ }^{\circ}\text{C}$) corresponds to the bulk melting point of the amine. This peak is present in the thermogram of the pure adsorbate in the absence of the graphite substrate. The additional peak with an onset at $-20.9\text{ }^{\circ}\text{C}$ (peak at $-17\text{ }^{\circ}\text{C}$) is neither present in the thermogram of the pure amine nor the bare graphite and hence arises from the interaction of the amine on the graphite.

Other closely related simple alkyl species, including alkanes, alcohols, carboxylic acids, alkenes, and phenyl alkanes, adsorbing on graphite all show a similar DSC transition to that at $-20.9\text{ }^{\circ}\text{C}$. Diffraction studies have been able to assign these transitions to the melting of a 2D solid layer. Due to the close similarity of the transition seen here for the amines and all these other alkyl species, the transition at $-20.9\text{ }^{\circ}\text{C}$ is therefore assigned to the melting of an adsorbed solid monolayer that coexists with the bulk liquid at this temperature. We therefore conclude that heptylamine forms a solid monolayer in coexistence with the liquid amine.

The enthalpy of melting of the monolayer can be determined from the area under this monolayer melting peak and is found to be approximately 0.40 joules per gram of graphite. This compares with values for alkanes, alcohols, and carboxylic acids of (typically) 0.2, 1.0, and 0.5 joules per gram of graphite, respectively. Clearly there is stronger hydrogen bonding in this amine monolayer than the related alkane, but this extra bonding is not as strong as for alcohols or carboxylic acids. This trend in behavior is also observed in the strength of hydrogen bonds involving oxygen or nitrogen atoms in the bulk materials.¹⁴

Figure 2 presents a summary of the results, bulk and monolayer melting points, for all the members of the homologous series from C_5 to C_{16} indicating that all of these linear amines with alkyl chains of C_6 or longer form solid monolayers coexisting with their bulk liquids. However for the shortest member of the series investigated, C_5 , no evidence of a solid monolayer that exists at temperatures above the bulk melting

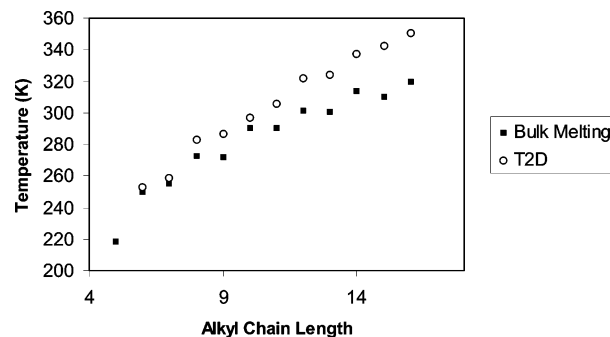


Figure 2. The variation in monolayer and bulk melting points as a function of alkyl chain length.

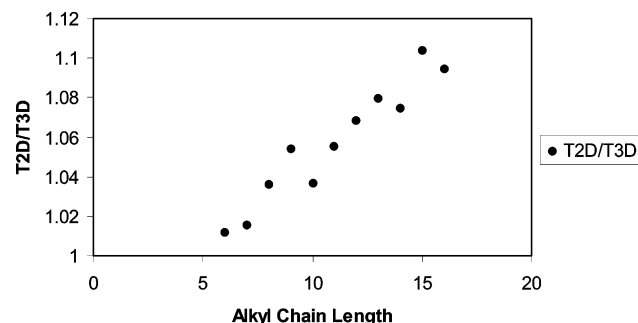


Figure 3. Variation of the ratio of monolayer and bulk melting points, T_{2D}/T_{3D} , as a function of alkyl chain length.

point could be found in these measurements. This behavior is very similar to that of adsorbed alkanes on graphite.¹⁵

Although many alkanes form a solid monolayer on graphite that coexists with the liquid, the pentane monolayer is anomalous. For pentane, the monolayer melting transition is not observed above the bulk melting point. However, previous calorimetric and diffraction studies have demonstrated that there is a solid monolayer of pentane on graphite. When only small quantities of pentane are present as small crystals, the bulk melting point is depressed.¹⁶ This movement of the bulk melting point enables the structure and melting behavior of the adsorbed monolayer to be identified. The pentane monolayer melts at the same temperature as the bulk.

Figure 3 illustrates the variation in the ratio of the monolayer and bulk melting point. For the longer chains this ratio is approximately 1.1, again very similar to the adsorbed alkane case. This is in accordance with expectations—amines with very long alkyl chains are essentially perturbed alkanes and thus we expect to recover alkane behavior for the longer homologues. It appears that this limit is attained for amines with carbon chains of 15 or 16 atoms. However for the shorter chains we see that the monolayer melting point progressively approaches that of the bulk material, suggesting that these adsorbed layers are less stable than the longer homologues.

Ammonia represents the shortest member of the amine series. Although not investigated here it is useful to recall the adsorption behavior of ammonia on graphite. Previous work, incorporating a number of techniques, including adsorption isotherms, neutron diffraction and incoherent scattering, atom scattering, and computer simulations, have been used to investigate the behavior of ammonia on graphite.^{17–23} Ammonia is of particular interest as it is a strongly dipolar species, and the large cohesion energy of polar molecules is expected to hinder the wetting of nonpolar solids.²¹ The experimental diffraction data do indeed appear to support this expectation. Instead of the saw-tooth line shapes characteristic of solid adsorbed layers^{24,25} the diffraction peaks are symmetrical and occur at the same position and with the

same relative intensities as those of bulk ammonia.^{18,23} This clearly indicates that no solid monolayer is formed, rather the ammonia does not wet the graphite and forms 3D crystallites. Interestingly it appears that the liquid ammonia will wet the graphite surface with more adsorption occurring at higher temperatures.

This unusual behavior of ammonia is in contrast to other adsorbed dipolar species such as the methyl halides, CH_3X , where $\text{X} = \text{F}, \text{Cl}, \text{Br}$, and I .^{26–30} All these dipolar species form well-ordered solid monolayers; in some cases more than one adsorbed layer phase is reported, showing the characteristic asymmetric diffraction peak line shape of a 2D layer. Interestingly, the dipole moments of these methyl halides (F) 1.858, (Cl) 1.896 D, (Br) 1.82 D, and (I) 1.64D, are somewhat larger than that of ammonia (1.471 D). This may suggest that dipoles alone are not responsible for the differences in behavior and that additional interactions such as hydrogen bonding between the ammonia molecules is a key contribution. In short, these previous studies demonstrate that solid ammonia does not like to wet the graphite surface.

Hence we conclude that linear amines represent a competition of effects. The alkyl chain would prefer to adsorb and form a solid monolayer. However, the amine group does not prefer to wet the surface in the solid state due to strong inter-amine interactions, dipolar and hydrogen bonding. For shorter chains the amine group is the dominant influence and the materials do not show any solid monolayer. However, for longer alkyl chains this unfavorable influence is dominated by the nature of the hydrocarbon carbon chain.

Using the measured enthalpies, from the areas under the monolayer melting peaks in the thermograms, and an estimate of the area per molecule (based on the equivalent alkane with one extra carbon atom to include the NH_2 group), we can estimate the monolayer melting enthalpy. For example, for decylamine this enthalpy is calculated to be approximately 7 kJ/mol. From this enthalpy value we can estimate the monolayer melting entropy to be $23.3 \text{ J mol}^{-1} \text{ K}^{-1}$. This value is of the same magnitude, but somewhat larger than the monolayer melting entropies for either ammonia or krypton on graphite, reported as $14.6 \text{ J mol}^{-1} \text{ K}^{-1}$ and $6.3 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively,²¹ but much smaller than the results of computer simulations of ammonia would suggest ($10\,000 \text{ J mol}^{-1} \text{ K}^{-1}$). A moderate increase in the enthalpy of monolayer melting of decylamine than ammonia is expected as the entropy of melting of alkyl species increases with alkyl chain length. However, due to the relatively large uncertainty of estimating the background in our DSC thermograms we are unable to obtain precise values of the monolayer melting enthalpies and take the values given here as estimates only. We cannot identify any significant variation in the monolayer melting enthalpies with alkyl chain length.

Careful investigation indicates that nonylamine shows an additional peak in the thermograms at approximately 5°C above the bulk melting point and prior to the monolayer melting (at approximately 17°C), as illustrated in Figure 4. This additional peak is more clearly resolved from the bulk melting peak in the lower cooling trace of Figure 4. This additional feature is much weaker than the monolayer melting transition, and so we conclude that it does not arise from melting/freezing of a bilayer³¹ but from some solid–solid phase transition, such as a rotator phase, observed with other alkyl species⁷ and the bulk amines. Only the thermograms of nonylamine show these additional transitions at temperatures above the bulk melting point. The other monolayers may also have such transitions but

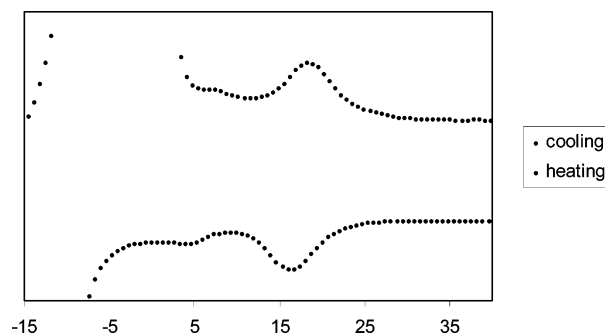


Figure 4. DSC thermograms of approximately 40 monolayers of nonylamine adsorbed on graphite in both heating (top) and cooling (bottom).

they may be too close to the monolayer or bulk melting points to be observed.

Conclusion

We conclude that the adsorption of linear amines is best understood as the competition of two effects arising from the nonwetting behavior of the NH_2 group and the adsorption of the alkyl chains. All the longer linear amines from C_6 to C_{16} form a solid monolayer that coexists with the bulk liquid adsorbate when adsorbed on graphite. However, the shorter homologues are dominated by the NH_2 group and do not show pre-solidification. There is evidence for strong hydrogen bonding in these solid monolayers as would be expected from bulk behavior and the chemical group present. Additional solid–solid phase transitions are observed in particular cases.

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