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Molecular Orientation of Carboxylic Acids Adsorbed on Graphite from the Liquid

Stuart M. Clarke, Akira Inaba[1], Robert K. Thomas[2] and Joe Fish[2]

Department of Chemistry and BP Institute, Madingley Rise, Madingley Road, Cambridge, CB3 0HE, UK
[1]*Department of Chemistry and Research Center for Molecular Thermodynamics, Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan*
[2]*Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ, UK*

We present incoherent elastic neutron scattering and calorimetry data from simple monocarboxylic acids, C9, C14 and C16, adsorbed from their liquids to the graphite surface which indicate the formation of solid monolayers with molecules which are predominantly upright.

KEYWORDS: neutron scattering, calorimetry, adsorbed monolayer, molecular orientation, solid-liquid interface

§1. Introduction

Monolayers adsorbed from liquids and solutions to solid surfaces are central to many academic and industrial problems. The structure and orientation of the molecules in the adsorbed layer can have a profound influence on the properties. For example, recent sum-frequency spectroscopy has indicated that the more effective lubricants are those with the more ordered adsorbed layers.[1)] However, it is very difficult to investigate these adsorbed layers as they are sandwiched between two bulk phases (the liquid and the solid) making them inaccessible. We have been developing a number of approaches[2–9)] to probe these adsorbed layers, including sensitive calorimetry and neutron scattering and have demonstrated that many simple molecules, *e.g.* linear alkanes and alcohols, form crystalline layers on graphite from their liquids and from binary solutions. In all of the cases examined so far the orientation of the molecules has been such that the long axes of the molecules are parallel to the surface. To date we have only investigated one carboxylic acid, dodecanoic acid (C12), and this also lies flat on the surface.[6)]

In this work we report incoherent elastic neutron scattering and calorimetry data that indicate that other carboxylic acids are inclined relative to the surface and, in some cases, are essentially perpendicular to the surface.

§2. Experimental

The experimental details of neutron scattering[2)] and DSC measurements[4)] have been described elsewhere. The substrate is a commercial graphite, Papyex, with a specific surface area of 27 m^2/g determined by nitrogen adsorption. When dosing the surface it is convenient to use equivalent monolayers, the amount of material required to cover a complete monolayer when the molecules are flat on the surface. This requires an estimate of the specific surface area of the substrate and the adsorbate. In this study, we assume that the monolayers on the graphite surface are homogeneous; the diffraction measurement then gives precise values of the surface areas per molecule in good agreement with those from DSC and adsorption isotherms. The size of the domains of the crystal is typically 150-200 Å based on the line shape analysis of similar systems.[6–9)] We have estimated the specific surface area of the acid molecules following the approach of Groszek.[10)]

§3. Results and Discussion

3.1 DSC

The DSC curve for approximately 50 monolayers of tetradecanoic acid adsorbed on graphite showed two transitions: one at 53.8°C which corresponds to bulk melting (literature value 54.4°C[11)]). The smaller peak at 86.6°C, which is not present for pure graphite or pure tetradecanoic acid, is attributed to the melting of an adsorbed layer, as observed with many other similar adsorbed species. The enthalpy of the monolayer melting is of the order of 0.5 J/g, larger than that typical of adsorbed alkanes (0.2 J/g). Here we have expressed enthalpy in Joules per gram of graphite as this avoids any assumptions concerning specific surface areas of the substrate and adsorbed layer required to convert to J/mol. We attribute the enhanced stability of the acid mono-

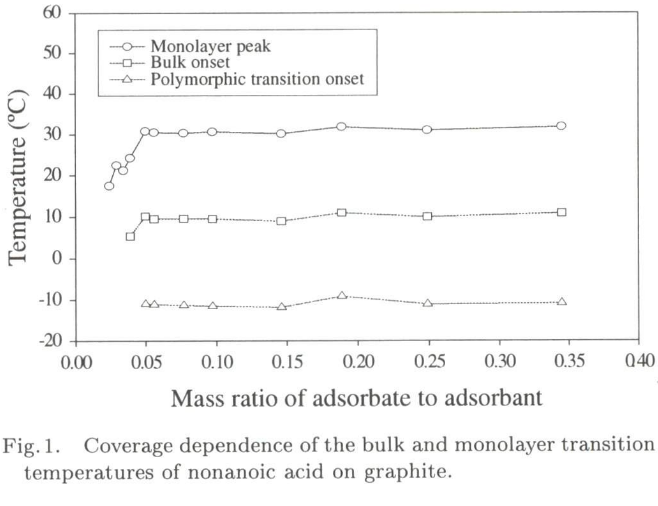

Fig. 1. Coverage dependence of the bulk and monolayer transition temperatures of nonanoic acid on graphite.

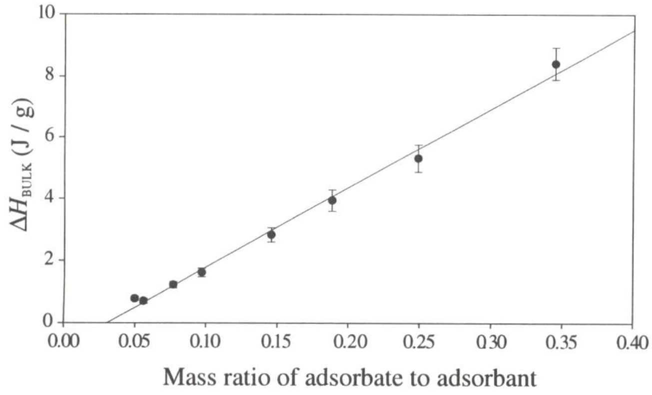

Fig. 2. Coverage dependence in the melting enthalpy of bulk nonanoic acid transition.

layer relative to alkanes to additional hydrogen bonding within the layer which is not possible with simple linear alkanes. Similar results were obtained for the other acids C9 and C16 clearly indicating the formation of similar solid monolayers for these materials.

Figure 1 presents the coverage dependence of the bulk and monolayer transition temperatures for nonanoic acid (C9). In addition to the bulk melting transition, nonanoic acid shows a bulk solid-solid phase transition. The x-axis is expressed in terms of the ratio of grams of adsorbate to grams of substrate. At very low coverage no bulk, polymorphic transition or monolayer peaks were evident. From a coverage of 0.02 a monolayer peak appears, which moves to higher temperatures until settling at a coverage of 0.05. The bulk peaks, melting and solid-solid transitions, also first begin to appear at approximately this coverage of 0.05. The bulk melting enthalpy increases thereafter with the mass ratio of adsorbate to adsorbant as shown in Fig. 2. This behaviour is precisely that expected if bulk condensation occurs after formation of a solid monolayer.

We can estimate the coverage required to form a complete monolayer from this calorimetry data from the intercept with the x-axis in Fig. 2 and the amount of adsorbate required to form a complete monolayer. Both these measures, the first appearance of bulk material and the completion of the monolayer, give a monolayer composition of approximately 0.05 g/g. This value corresponds to an estimated area per molecule of 15 Å^2. From the bulk crystal structures of the carboxylic acids we can estimate the surface areas occupied by a single molecule if flat (approximately 100 Å^2) or upright (25 Å^2) on the surface. The experimentally determined surface area is much closer to that of an upright molecule than one flat on the surface. Indeed, the specific surface area is even small enough to indicate that there is an upright monolayer of dimers on the surface (which would give a surface area of approximately 13 Å^2). This dimerisation is favoured by intermolecular hydrogen bonding of the acids, and would be very similar to that observed in the bulk crystals of carboxylic and fatty acids.[12] It is important to note that this approach only indicates the total amount adsorbed before bulk condensation begins. We see no indication of other transitions from the individual monolayers. If a multilayer is adsorbed it must be formed as a single entity.

Similar measurements of the coverage dependence for hexadecanoic acid indicate that the monolayer is completed at a coverage of approximately 0.03 g/g or a surface area per molecule of 40 Å^2. This again suggests a predominantly upright orientation of the molecules in the adsorbed layer. However, it should be noted here that such calorimetric evidence only gives indirect information about the area per molecule. Other effects, such as the coverage dependence of heats of adsorption and the reorganisation of adsorbed layers, may be involved in the measured enthalpy, which affects the estimated area substantially.

3.2 Incoherent elastic neutron scattering

We have previously outlined the INS experimental approach indicating how the measured intensity can be used to obtain a direct measure of the amount of solid adsorbate as a function of temperature.[3] The narrow energy resolution required for the present experiments was obtained either with a backscattering instrument IN10 at ILL, Grenoble, with an energy resolution of 1.5 μeV or with a time-of-flight spectrometer LAM-80ET at KEK, Tsukuba, with a resolution of 15 μeV.

The formation of a solid monolayer was clearly indicated by the residual scattering intensity above the bulk melting point. Such behaviour is illustrated in Fig. 3 for tetradecanoic acid. The large fall in intensity at a temperature of 328 K corresponds to most of the adsorbate melting at the bulk melting point. However, the intensity does not fall to background but there is a residual intensity arising from the solid adsorbed layer. This layer is seen to melt at 355 K. The relative intensities of scattering at low temperatures, when all the adsorbate is solid, and that in the temperature region where only the

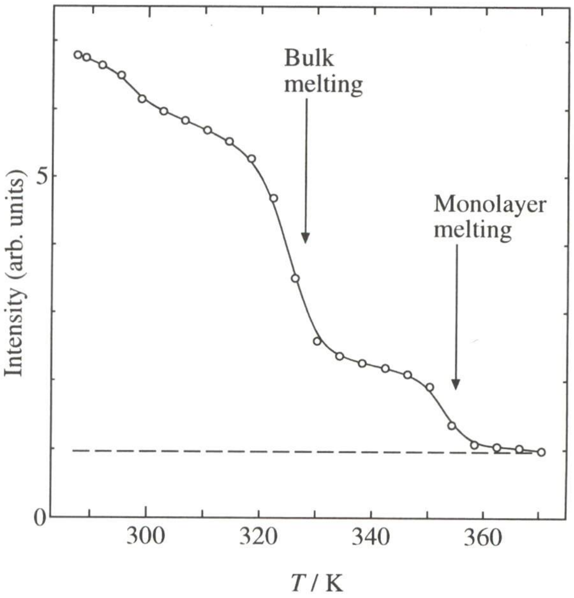

Fig. 3. Incoherent elastic neutron scattering intensity as a function of temperature for tetradecanoic acid/graphite obtained on IN10 at ILL. The background level is indicated.

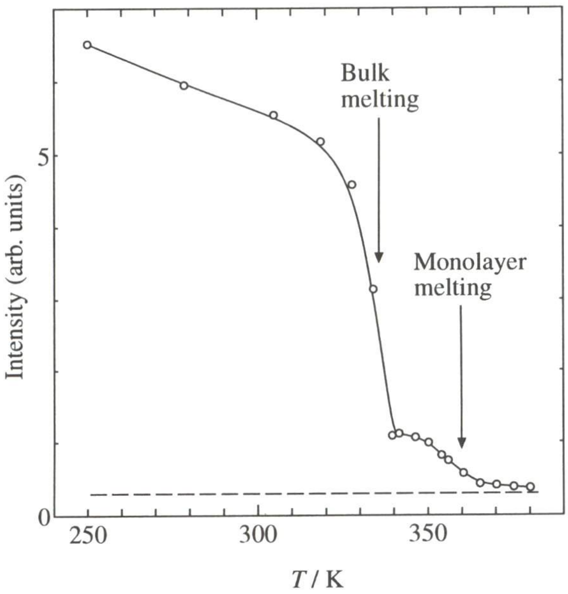

Fig. 4. Incoherent elastic neutron scattering intensity as a function of temperature for hexadecanoic acid/graphite obtained on LAM-80ET at KEK. The background level is indicated.

monolayer is solid are a measure of the amount of acid in the solid monolayer. From this quantity we can again estimate the area per molecule in the solid monolayer. For tetradecanoic acid the surface area per molecule is determined to be approximately 56 Å^2 which lies between that of an upright and a flat molecular orientation, possibly suggesting a tilted molecule. Little can be said about the small change around 300 K seen in Fig. 3. According to the literature,[11] however, there is no solid-solid phase transition in the bulk C14 acid. It could be of monolayer origin.

From similar measurements made with hexadecanoic acid (Fig. 4) the surface area per molecule is determined to be 60 Å^2. This is somewhat larger than the value determined above from calorimetry data of 40 Å^2. The melting temperatures of the bulk solid and the monolayer of C16 acid were 336 K and 360 K, respectively. At this stage, we are not able to explain why C9, C14 and C16 acids exhibit different behaviour from C12 acid. However, we think that it might be a combination of chain length and the odd-even effect. If odd and even are different, as they are for short alkanes, then C9 and C12 could be different. C12 is shorter than C14 and C16. In the case of alkanes, C12 is different in the phase behaviour from other even alkanes.[4,5] Diffraction measurements are needed to give more detailed structural information.

§4. Conclusions

In this work we have clearly identified the formation of solid monolayers for monocarboxylic acids of C9, C14 and C16. The melting points are approximately 10% higher than the bulk melting points, as reported for other alkanes and alcohols. In addition we have estimated the specific surface area per molecule using calorimentry and incoherent neutron scattering measurements. These results suggest that, far from being parallel to the surface like alkanes and alcohols, there is good evidence that the molecules, if not perpendicular to the surface, are at least strongly tilted. It is interesting to note that a recent STM study showed that the C14 and C16 acids adsorbed from the solution lie flat on the graphite surface.[13]

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