Crystalline Monolayer of Dodecanoic Acid Adsorbed on Graphite from *n*-Heptane Solution

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The combination of incoherent elastic and quasielastic neutron scattering with neutron diffraction has been used to show the formation of a two-dimensional crystalline monolayer of dodecanoic acid in equilibrium with heptane solution. The molecules in the monolayer are found to be lying with their long axes parallel to the surface. This solid monolayer melts at approximately 1.15 times the melting point of the bulk solution.

Introduction

The adsorption of alkanols and carboxylic acids as solutes in liquid hydrocarbon solutions onto solid surfaces has been extensively studied by calorimetry and isotherm measurements.[1,2] In several cases preferential adsorption of the solute has been observed with the formation of a monolayer, which may be solid- or liquid-like. These monolayers have an important role in many important interfacial phenomena such as detergency and lubrication. Detailed characterization of these adsorbed layers is difficult largely because of the presence of the solution. Recently structural information from techniques such as specular neutron reflectivity[3] and scanning tunneling microscopy (STM)[4,5] has started to become available. However, reflectivity measurements only provide structural information normal to the plane of the interface, and there is still often significant uncertainty over the interpretation of the results from STM techniques.

The difficulty of applying scattering techniques to the solid/liquid interface is partly one of adequate penetration to observe the buried interface and partly one of distinguishing the surface layer from molecules forming the bulk liquid. This makes it desirable to reduce the quantity of the bulk liquid phase to a minimum, but the question then arises as to how much material constitutes this minimum. In the case of a solute expected to adsorb relatively strongly, any influence of the surface on the remaining solution should be small. We have chosen in the present work to have the equivalent of about 10 molecular layers of solution with enough solute to have a reasonable mole fraction in the solution, even in the presence of an adsorbed layer. The combination of the two neutron scattering techniques used in this work can provide unambiguous information on both the state and absolute composition of an adsorbed layer as well as in-plane structural information.

In this paper the adsorption behavior of dodecanoic acid from *n*-heptane solution is investigated using incoherent elastic neutron scattering in combination with coherent neutron diffraction. This combination of these techniques is essential for characterizing these complex multicomponent systems. The incoherent elastic scattering technique is able to identify the formation of any solid monolayer over a wide temperature range much more quickly than diffraction. Significantly, incoherent elastic neutron scattering can identify the fraction of solute and solvent present as a solid as a function of temperature, allowing the absolute composition of the monolayer to be determined. The incoherent scattering technique also provides an estimate of the density of the surface layer. It is extremely difficult to interpret surface diffraction patterns not knowing the monolayer density. In this paper coherent neutron diffraction provides structural identification and characterization of the solid material indicated by the incoherent elastic scattering measurements.

Experimental Section

This work incorporated a combination of two techniques, incoherent quasielastic neutron scattering and neutron diffraction. Only a brief outline of the techniques is presented here. Full details can be found elsewhere.

The apparatus and procedures for the neutron diffraction experiments have been described elsewhere.[6,7] The instrument used was D1B at the Institut Laue-Langevin, Grenoble, France,[8] with a wavelength of 0.252 nm. Scattering from crystalline two-dimensional adsorbed layers gives rise to diffraction peaks[9,10] which can be used to determine the structure of the layer in a manner analogous to diffraction from three-dimensional crystals. Diffraction from two-dimensional crystalline structures gives rise to peaks with a characteristic "sawtooth" line shape,[11,12] while fluid phases give rise to very broad, symmetrical diffraction peaks. The diffraction pattern from adsorbed material is obtained by subtraction of the scattering

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from the substrate alone from that of the substrate and adsorbed material together. For these experiments the materials were deuterated to minimize the background from incoherent scattering of protonated samples.

Full details of the technique of incoherent quasielastic neutron scattering can be found elsewhere,[13] but, for the purposes of this experiment, we restrict ourselves to incoherent elastic scattering. We have described the application of this to the adsorption behavior of a number of pure materials, including *n*-heptane, *n*-dodecane, 1-dodecanol, and dodecanoic acid in a previous paper,[14] and shown that it is particularly sensitive to solid monolayer material.

The quasielastic scattering experiments reported here were performed on two instruments, a time-of-flight spectrometer LAM-80ET at the National Laboratory for High Energy Physics, Tsukuba, Japan (KEK), and IN10 at the Institute Laue-Langevin.

The energy resolution of LAM-80ET[15] was approximately 15 μeV. The data were collected as intensity as a function of scattered neutron energy at Q values of 2.5, 8.4, 12.1, and 16.5 nm^{-1}. Q, the momentum transfer, is defined here as $(4\pi \sin \theta)/\lambda$, where λ is the wavelength of the incident beam and 2θ the scattering angle. The backscattering instrument IN10[8] has a very narrow energy resolution of approximately 1.5 μeV. In the experiments reported here the incident wavelength was 0.6275 nm with both monochromator and analyzer crystals of Si(111). The Doppler drive was turned off such that only elastically scattered neutrons reached the detectors. For typical fluid phases, with diffusion coefficients on the order of 5 $\times$ 10^{-9} m^2 s^{-1},[16,17] there will be a negligible contribution from any fluid phases to the elastic peak. The configuration used allows very rapid data collection because the measured intensity is approximately proportional to the amount of solid material present in the sample. No energy analysis of the scattered neutrons was made in the IN10 experiment.

In this work where we are principally concerned with the evolution of the intensity of the elastic incoherent scattering with temperature. The high resolution of IN10 enables us to obtain this information directly. LAM 80ET, with its lower resolution, gives both quasielastic and elastic incoherent scattering, and we must determine the contribution of the quasielastic component to obtain the elastic scattering contribution. However, this procedure has the advantage that we can estimate the diffusion coefficients of any fluid phases from the quasielastic scattering.

The adsorbent used in these experiments was recompressed exfoliated graphite Papyex (Le Carbone Lorraine) with a specific surface area of 20 m^2 g^{-1} determined by adsorption of nitrogen. Deuterated *n*-heptane was obtained from Agros Organics with a quoted deuteration level of >99%, and deuterated dodecanoic acid was prepared according to the method of ref 18 with a deuteration level of approximately 90 $\pm$ 3%. The protonated hydrocarbons were obtained from Aldrich. The graphite substrates were outgassed under vacuum in an oven before known quantities of the adsorbates were added as solid or liquid under an inert atmosphere (He) and annealed. The annealing protocol was either (a) to add liquid heptane by microsyringe and anneal close to its boiling point and then add solid dodecanoic acid and then anneal at the same temperture close to the boiling point of heptane or (b) to add solid dodecanoic acid, anneal at about 200 °C, then add liquid heptane, and anneal at just below the boiling point of heptane. Both routes gave similar behavior, which is a good indication that the system was at equilibrium.

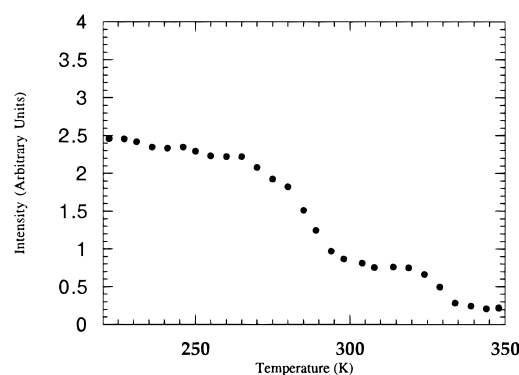The bulk melting behavior of mixtures of *n*-heptane and

Figure 1. Incoherent elastic scattering as a function of temperature of 0.4 mmol of dodecanoic-h_{24} acid and 2.4 mmol of heptane-d_{16} adsorbed on 3.24 g of Papyex. These data were obtained from IN10 at the Institut Laue-Langevin.

TABLE 1: Incoherent Cross-Sections for the Pure Materials Used in This Work

molecule	incoherent cross-section (barns)	molecule	incoherent cross-section (barns)
heptane-h_{16}	1279	dodecanoic-h_{24} acid	1918
heptane-d_{16}	32	dodecanoic-d_{24} acid	49

dodecanoic acid was investigated as a function of composition. Mixtures of the appropriate composition in screw-cap bottles sealed with Parafilm were suspended in a thermostatically controlled water bath with glass sides. The temperature was maintained to within an absolute value of 0.5 K.

Results

A. Incoherent Elastic Neutron Scattering. The incoherent signal from protonated samples is much more intense than for deuterated samples. Two mixtures were used, a mixture of dodecanoic-d_{24} acid, $C_{12}D_{24}O_2$, in heptane-h_{16}, C_7H_{16}, with scattering predominantly from the heptane, and dodecanoic-h_{24} acid, $C_{12}H_{24}O_2$, in heptane-d_{16}, C_7D_{16}, with scattering predominantly from the dodecanoic acid. By this means the amount of solid heptane and dodecanoic acid at each temperature could in principle be determined separately. The actual contribution to the incoherent elastic scattering from each component depends upon the incoherent cross-section of the individual molecules. Table 1 gives the incoherent scattering cross-sections from the molecules used in this study. The protonated samples used are taken to be fully protonated. However, the level of deuteration in the "deuterated" samples is important because even a small amount of protonated material will greatly increase the incoherent scattering from that component. On the basis of the levels of deuteration of the individual materials and the relative mole fractions, the contribution of dodecanoic acid to the scattering from the heptane-h_{16}/dodecanoic-d_{24} acid mixture is calculated to be approximately 3%. Similarly, the contribution from heptane to the heptane-d_{16}/dodecanoic-h_{24} acid mixture is approximately 10% of the total scattering.

Figure 1 shows the intensity of the incoherent elastic peak as a function of temperature for 0.4 mmol of dodecanoic-h_{24} acid and 2.4 mmol of heptane-d_{16}, adsorbed on 3.24 g of graphite. This corresponds to approximately 10 monolayers of heptane and 3 monolayers of dodecanoic acid. The scattering in the figure is predominantly from solid dodecanoic acid because this is the protonated component. At the lowest temperatures in the figure all of the dodecanoic acid is solid, giving a strong elastic signal. At a temperature of 285 K,
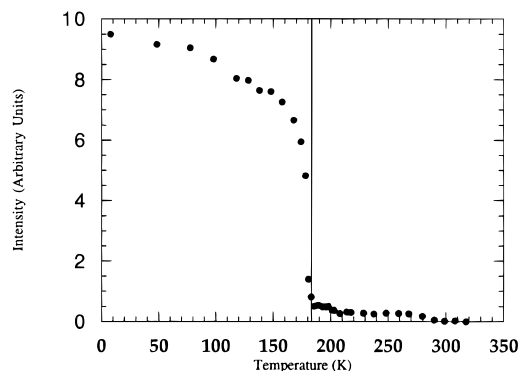
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Figure 2. Incoherent elastic scattering as a function of temperature for 10.84 mmol of heptane-h_{16} and 1.95 mmol of dodecanoic-d_{24} acid adsorbed on 14.61 g of Papyex. The vertical line indicates the melting point of bulk heptane. These data were obtained from the LAM-80ET instrument at KEK with $Q = 14.3$ nm^{-1}.

substantially below the pure bulk melting point (317 K), the intensity has fallen significantly, although above this temperature and above the bulk melting point up to 328 K there is a significant residual intensity. We have shown in a previous paper that for pure dodecanoic acid and heptane, which do not have rotator phases in the bulk, that the intensity of the elastic scattering can be related approximately to the fraction of material that is not undergoing translational diffusion, i.e., solid material.[14] With this particular sample, the elastic peak intensity is related to the fraction of solid dodecanoic acid only. The residual intensity above 285 K cannot be associated with bulk solid dodecanoic acid because this would melt at the bulk melting point. We therefore tentatively identify it as a solid monolayer. This solid monolayer survives until a temperature of approximately 328 K, and then it too melts with the elastic scattering falling to the level of the graphite background. At low temperatures there is a fall in intensity of the elastic peak at a temperature of 183 K, not shown in the figure, due to the melting of bulk heptane. This appears partly because the sample is not completely deuterated and partly because the incoherent scattering cross-section of deuterium is not zero.

Similar incoherent elastic neutron scattering data measured on LAM-80ET for a mixture of 10.84 mmol heptane-h_{16} and 1.95 mmol of dodecanoic-d_{24} acid adsorbed onto 14.61 g of graphite as a function of temperature is presented in Figure 2, where the background has been subtracted. The relative amounts of heptane, dodecanoic acid, and graphite in this experiment are the same as those of Figure 1. The data at $Q = 12.1$ and 16.5 nm^{-1} have been combined to obtain better statistics. The intensity of the elastic component has been extracted from a fit to the full quasielastic spectrum of scattered neutrons. At the lowest temperatures in this figure all of the heptane and dodecanoic acid are solid. As the temperature is increased, there is evidence of premelting of the heptane as the bulk melting point of heptane is approached. Just above this bulk melting point not all of the heptane has melted. There is a residual amount which corresponds to about 0.2 monolayers taking the value of the area per molecule from ref 14. This amount of solid heptane melts at a temperature of 205 K, which is very close to that of a solid monolayer adsorbed from the pure liquid.[14] The fall in intensity at a temperature of 285 K corresponds to the melting of the dodecanoic acid to form a solution with heptane. This feature is not very strong and is only evident because the dodecanoic acid is not fully deuterated.

B. Incoherent Quasielastic Neutron Scattering. Figure 3 shows a full spectrum, including background, of scattered neutrons measured on LAM-80ET at a temperature of 190.9 K
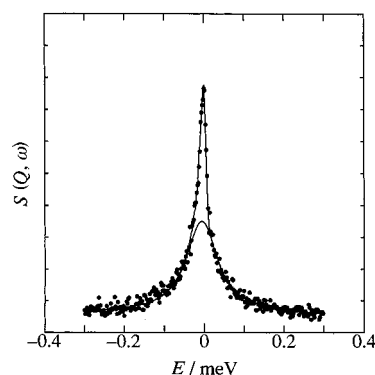

Figure 3. Incoherent quasielastic neutron spectrum for a mixture of 10.84 mmol of heptane-h_{16} and 1.95 mmol of dodecanoic-d_{24} acid adsorbed onto 14.61 g of graphite at a temperature of 190.9 K. These data were obtained from the LAM-80ET instrument at KEK.

from a mixture of 10.84 mmol of heptane-h_{16} and 1.95 mmol of dodecanoic-d_{24} acid adsorbed onto 14.61 g of graphite. The Q value for this spectrum is 12.1 nm^{-1}.

The width of the elastic peak is determined by the experimental resolution. For a three-dimensional fluid undergoing translational motion, the profile of the quasielastic peak can be approximated by a Lorentzian of the form[17]

$$S(Q,E) = \frac{F(Q)}{\pi} e^{-Q^2\langle u^2\rangle} \frac{\hbar DQ^2}{(\hbar DQ^2)^2 + (E - E_0)^2} \quad (1)$$

where $\hbar$ is Planck's constant divided by 2π, D is the diffusion coefficient, and E and E_0 are the energies of the incident and scattered neutrons and $E-E_0$ is the energy exchange on scattering. $F(Q)$ is the elastic incoherent structure factor (EISF), and $\exp(-Q^2\langle u^2\rangle)$ is a Debye$-$Waller factor.

The form of the scattering for a two-dimensional fluid "bound" to a substrate is similar to eq 1 except for a geometrical factor which accounts for the orientation of the surface.[17] The substrates used in this study are powders with a distribution of surface orientations, and the observed scattering is a sum of contributions from all of the surfaces. Previous workers[17] have shown that the effect of the distribution of orientations for our particular substrate, Papyex, is simply to introduce a numerical prefactor of 1.7 into eq 1.

On the basis of this analysis, the translational diffusion coefficient of the atoms in the sample can be obtained from the full width at half-maximum of the broad quasielastic peak, $2\hbar DQ^2$. The width of the best fit to the broad quasielastic peak, shown as a continuous line in Figure 3, corresponds to a diffusion coefficient of 4.5×10^{-10} m^2 s^{-1}. This least-squares fitting procedure also gives the intensity of elastic scattering, shown in Figure 2, by removing the contribution of the quasielastic scattering from the total scattering. Three-dimensional fluid heptane at 298 K has a diffusion coefficient of approximately 3.12×10^{-9} m^2 s^{-1}.[19] There are several possible reasons for the difference between these values, particularly the temperature difference and possibly also any two-dimensional nature of a bound fluid.

C. Neutron Diffraction. The neutron diffraction pattern from 0.405 mmol of dodecanoic-d_{24} acid adsorbed on 9.85 g of Papyex at 275 K is given in Figure 4b. The neutron diffraction pattern from 0.405 mmol of dodecanoic-d_{24} acid and 0.656 mmol of heptane-d_{16} adsorbed on 9.85 g of Papyex at 275 K is given in Figure 4a. The graphite background has already been subtracted in preparing these patterns. The feature at $2\theta = 44°$ arises from imperfect graphite subtraction. The
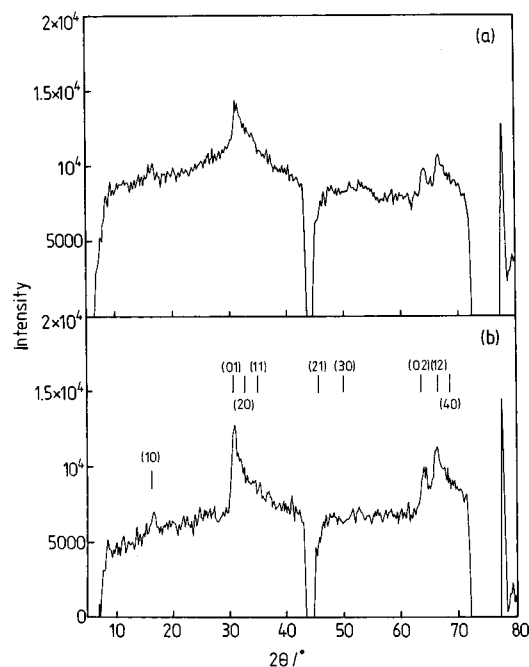
Figure 4. (a) Experimentally determined diffraction pattern of dodecanoic-d_{24} acid and heptane-d_{16} adsorbed on graphite at a temperature of 275 K. The coverage is approximately one monolayer of dodecanoic-d_{24} acid and one monolayer of heptane-d_{16}. The incident wavelength is 0.252 nm, and the graphite background has been subtracted in producing these patterns. (b) Experimentally determined neutron diffraction pattern of dodecanoic-d_{24} acid adsorbed on graphite at a temperature of 275 K. The coverage is approximately one monolayer. The tick marks in Figure 4b correspond to the indexing of the experimental reflections with a unit cell with parameters $a = 0.893$ nm, $b = 0.48$ nm, and $\nu = 90°$.

TABLE 2: Positions and Relative Intensities of Principal Reflections in Figure 4b[a]

reflcn	exptl 2θ	rel intens	calcd 2θ	index
1	16.2	0.22	16.2	(1,0)
2	30.4	1.0	30.4	(0,1)
3	63.6	0.56	63.6	(0,2)
4	65.8	0.67	65.8	(1,2)

[a] This table also includes the calculated positions and index of reflections based on a unit cell with parameters $a = 0.893$ nm, $b = 0.48$ nm, and $\nu = 90°$.

flat background arises principally from the incoherent scattering from the adsorbed molecules, a weak contribution from the majority that are deuterated and a much stronger contribution from protonated impurities. The pattern in Figure 4b contains peaks with the characteristic "sawtooth" line shape of diffraction from an adsorbed monolayer.[11,12] The experimentally determined positions and relative intensities of the two-dimensional reflections are given in Table 2. The pattern in Figure 4a, the mixture, also contains the diffraction peaks from this two-dimensional layer but also has a broad peak, centered at a 2θ value of about 30°, which is typical of a fluid phase. Patterns from this mixture show that solid monolayer and fluid coexist up to 323 K. However, at 333 K and above (not shown) there is only a broad fluid-like peak and no evidence of a two-dimensional solid layer. This is in good agreement with the incoherent elastic scattering measurements where the adsorbed monolayer melts at 328 K.

D. Bulk Melting Points of Heptane and Dodecanoic Acid Mixtures. Figure 5 shows the experimentally determined melting points of *n*-heptane and dodecanoic acid mixtures as a
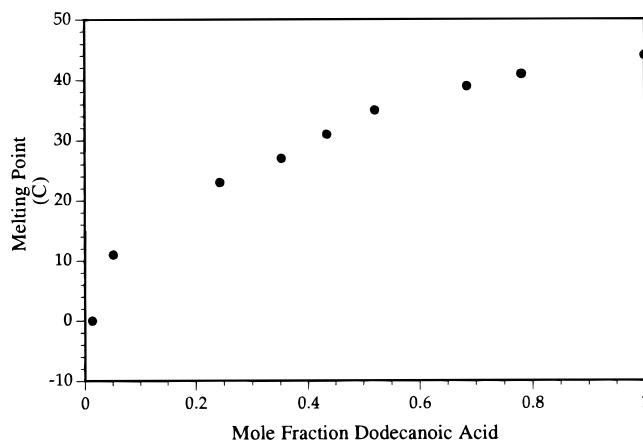

Figure 5. Variation of melting point with mole fraction of solutions of dodecanoic acid and *n*-heptane. The melting point of pure dodecanoic acid is also given in the figure.

function of the mole fraction of dodecanoic acid. The melting point of dodecanoic acid is progressively lowered by the addition of heptane.

Discussion and Conclusions

The result from the incoherent elastic scattering experiment, that the melting point of most of the dodecanoic acid to form a solution with heptane occurs at 285 K, is in good agreement with the melting point of a bulk mixture with the same overall composition, $x_2 = 0.143$ (289 K), given in Figure 5. If one monolayer of dodecanoic acid is on the surface, then the composition of the solution should be adjusted to $x_2 = 0.1$ with a bulk melting point determined from Figure 5 of 286 K, which is in even better agreement with the incoherent scattering results. The drop in intensity at a temperature of 285 K is therefore taken to arise from melting of the dodecanoic acid to form a solution with heptane.

Since the bulk solution must melt entirely above about 285 K, any residual dodecanoic acid can only be present as a solid monolayer. An estimate of the amount of solid dodecanoic acid just above 285 K can be made from the ratios of incoherent elastic intensity at this temperature and at a temperature of 220 K, where all of the dodecanoic acid is solid and all of the heptane liquid. This gives an amount of solid dodecanoic acid of 0.10 $\pm$ 0.015 mmol. As described above, approximately 20% of the surface is covered with heptane, leaving 80% covered with dodecanoic acid equivalent to a single monolayer with 0.84 $\pm$ 10 nm^2/molecule. This is in reasonable agreement with the area per molecule obtained from adsorption of dodecanoic acid from its liquid, 0.86 nm^2.[14] Although the error of this estimate is quite large, the value does indicate that the molecules are predominantly lying with their long axes parallel to the surface.

The melting point of the monolayer is 328 K, approximately 1.15 times the melting point of the bulk mixture. Thus, the melting point of this monolayer adsorbed from heptane solution is quite different from that of the monolayer adsorbed from pure liquid dodecanoic acid (342 K). For pure dodecanoic acid the melting point of the monolayer was approximately 1.1 times the bulk melting point. It is usually the case that adsorbed monolayers with a coverage at or less than unity melt below their bulk melting point,[6] although there are a few exceptions.[20] Solid monolayers that exist above the melting point of the bulk hydrocarbon have been reported.[14,21]

The scattering in Figure 2 arises predominantly from solid *n*-heptane, although there is a significant contribution from the

dodecanoic acid (approximately 2%) because this molecule is not entirely deuterated. The contribution to the scattering from the dodecanoic acid is seen in the drop in intensity at 285 K when the bulk solution is formed. The intensity change on melting of the solid dodecanoic acid monolayer at 328 K is too small to be observed. Below 220 K all of the dodecanoic acid is solid. Calculations based on the data in Figures 1 and 2 indicate that, within experimental error, there is no heptane contained in the solid monolayer above 285 K which is entirely dodecanoic acid.

The sawtooth shaped peaks in the diffraction pattern of Figure 4b clearly indicate that there is a crystalline two-dimensional layer on the graphite surface. These reflections can be indexed with a rectangular unit cell with parameters $a = 0.893$ nm, $b = 0.480$ nm, and $\nu = 90°$. A comparison of calculated and experimentally determined positions of reflections is given in Table 2, and the area of this cell is calculated to be 0.429 nm^2. This is almost exactly half the area expected for dodecanoic acid molecules with their long axes parallel to the surface, 0.86 nm^2, and that estimated from the results of the incoherent scattering measurements, 0.85 nm^2. The length of a fully extended C_{12} chain is expected to be around 1.7 nm, which is approximately twice the parameter a or 1.786 nm. The unit cell must therefore have parameters of at least $a = 1.786$ nm, $b = 0.480$ nm, and $\nu = 90°$. The absence of reflections indicating the larger unit cell is probably due to systematic absences arising from the space group of the unit cell. A full discussion of the space groups available to two-dimensional monolayers of molecules with particular symmetry elements is given in refs 6 and 9.

The diffraction pattern of Figure 4a clearly indicates that the monolayer reflections from the two-dimensional crystalline monolayer of dodecanoic acid, in Figure 4b, survive with the addition of liquid *n*-heptane. The broad peak in Figure 4a is interpreted as scattering from the liquid heptane. In other words, a crystalline monolayer of dodecanoic acid is coexisting with liquid heptane. The lattice parameters of the peaks from the crystalline dodecanoic acid monolayer appear to be essentially unchanged from those of pure dodecanoic acid, indicating that the molecules lie with their long axes parallel to the surface with an area of 0.86 nm^2/molecule. The melting point of the layer (between 323 and 333 K) is in good agreement with the incoherent elastic scattering measurements, 328 K.

Isotherm studies of long-chain alkanes, $C_{16}-C_{32}$, adsorbed from *n*-heptane solution onto a graphite interface[1,2,22] have reported the formation of aligned and close-packed molecular monolayers. Squalane, which has bulky side groups, is reported not to form such close-packed monolayers.[1] Other behavior such as the formation of mixed monolayers, 2D-eutectics,[22] and multilayer adsorption have also been identified. Ordered monolayers have also been reported for alcohols adsorbed from organic solution onto graphite.[2,5,23]

The results presented here support the same formation of close-packed monolayers with molecules lying with their long axis parallel to the surface as those reported by other authors.[5,24,25] A recent STM study[5] of the fatty acids, C_{17}, C_{19}, and C_{23}, adsorbed from organic solutions (phenyl octane, diphenyl sulfide, and 1,3,5-trimethyl-1,1,3,5,5-pentaphenyltrisiloxane) has identified lamellar structures with extended carbon chains oriented parallel to a lattice axis in the graphite basal plane. For these fatty acids, the chains are perpendicular to the lamellae and the layers are not registered with respect to the underlying graphite. Isotherm studies[24] of the simple fatty acids C_{10}, C_{12}, C_{14}, and C_{18} adsorbed from *n*-heptane onto graphite indicate that all form close-packed monolayers with their major axes parallel to the graphite. The close-packed monolayers of the carboxylic acids were found to be much less stable than the corresponding *n*-alkanes with the same number of carbon atoms, and this was attributed to "bulky" acid groups destabilizing the structure with respect to acid dimers surrounded by solvent molecules. Any structural conclusions from isotherm measurements are extremely indirect compared to those based on the incoherent elastic scattering data presented here.

A simple indicator of the stability of an adsorbed monolayer is the melting point of the adsorbed layer, T^{2D}, relative to the bulk melting point, T^{3D}. The results presented here for dodecanoic acid and elsewhere[14] for dodecane give the ratio of these melting points to be approximately 1.1 for both materials, indicating similar relative stabilities for acids and alkanes with the same number of carbon atoms. However, the absolute value of the melting point of the adsorbed layer of dodecanoic acid is approximately 50 °C higher than that of dodecane.

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