

Competitive Adsorption of Simple Linear Alkane Mixtures onto Graphite

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Received: July 10, 1998; In Final Form: October 20, 1998

The combination of differential scanning calorimetry and incoherent elastic neutron scattering has been used to demonstrate the formation of solid layers adsorbed onto graphite from pure alkanes and binary alkane mixtures. We report enthalpies and temperatures of the monolayer transitions for pure alkanes and mixtures and note that the solid monolayers melt at approximately 1.1 times the melting point of the bulk liquid or solution. In the mixtures the longer alkane is found to be preferentially adsorbed with the formation of a solid monolayer even when it is present as the minor component in the solution and when the carbon chain lengths differ by only a single CH₂ group.

Introduction

The adsorption of mixtures of simple molecules such as alkanes, alcohols, and carboxylic acids onto solid surfaces has been extensively studied by a number of techniques including calorimetry and isotherm measurements.^{1–3} In several cases preferential adsorption of the solute has been observed with the formation of a monolayer. These monolayers have a role in many important interfacial phenomena, but their characterization is difficult largely because of the presence of the solution. Recently, structural information from techniques such as specular neutron reflectivity⁴ and scanning tunneling microscopy (STM)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. As a result, even elementary information about the adsorbed layers, e.g., whether they are solid- or liquidlike, is still not available.

Applying scattering techniques to the solid/liquid and solid/solution interfaces to obtain structural information is a problem partly of having adequate penetration to the buried interface and partly of having the sensitivity to distinguish the surface layer from the bulk phases. In this respect the solid/liquid interface is quite distinct from the solid/vapor and liquid/vapor interfaces. The transmission problem makes it desirable to reduce the quantity of bulk liquid phase to a minimum, but the question then arises as to how little material constitutes the minimum amount to have the characteristics of the true bulk solution phase. This issue will be addressed later in the paper.

We have recently demonstrated^{6–8} that incoherent elastic neutron scattering is a powerful tool for identifying and characterizing monolayers adsorbed from pure materials and solutions. These results were supported by neutron diffraction measurements.^{7,8} A particular advantage of the incoherent neutron scattering technique when considering adsorption from multicomponent solutions is its ability to distinguish the individual behavior of each of the components.⁸ This neutron scattering technique can provide unambiguous information on both the state and absolute composition of an adsorbed layer as well as other information such as estimates of the area per molecule on the surface.^{7,8}

Although they provide detailed information, neutron scattering techniques are time-consuming and difficult measurements to make. It would be more convenient to be able to survey the temperature and composition behavior of the adsorbed systems with calorimetry. However, although such measurements identify the position and enthalpies of transitions of the bulk and monolayers, they are unable to distinguish the behavior of the individual components in a mixture.

In this paper the adsorption behavior of the linear alkanes, pentane (C₅), hexane (C₆), octane (C₈), nonane (C₉), decane (C₁₀), and dodecane (C₁₂), both as pure materials and as binary mixtures is investigated using incoherent elastic neutron scattering (INS) in combination with differential scanning calorimetry (DSC). The DSC technique characterizes these materials over a wide range of composition, coverage, and temperature in order to enable selection of the most effective incoherent elastic neutron scattering measurements for confirming the presence of solid adsorbate and for determining the absolute composition of the monolayers in the binary mixtures.

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Experimental Section

Only a brief outline of the INS and DSC techniques is presented here; full details can be found elsewhere.⁹

INS. 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 in contact with graphite, including *n*-heptane, *n*-dodecane, 1-dodecanol, and dodecanoic acid in a previous paper.⁷ The underlying principle is that the intensity of incoherent elastic scattering depends on the quantity of solid material present in the sample cell. The relative importance of motion other than translation on the incoherent elastic scattering intensity has been discussed previously.⁷ The technique was shown to be sufficiently sensitive to be able to observe submonolayer quantities of solid material in the presence of the equivalent of tens of monolayers of liquid.

The incoherent elastic scattering experiments reported here were performed on IN10 at the Institute Laue-Langevin, Grenoble, France. This backscattering instrument¹⁰ has a very narrow energy resolution of approximately 1.5 μeV . The incident wavelength was 0.6275 nm with both monochromator and analyzer crystals of Si(111). No energy analysis of the scattered neutrons was made in this experiment, so the Doppler drive was turned off such that only elastically scattered neutrons reached the detectors. For typical fluid phases of alkanes, with diffusion coefficients of about $5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$,^{11,12} there will be a negligible contribution from any fluid phases to the elastic peak. In this work we are principally concerned with the evolution of the intensity of the incoherent elastic scattering with temperature, and the high resolution of IN10 enables us to obtain this information directly. The intensity of incoherent scattering is particularly strong for protons, even relative to deuterons, which means that isotopic labeling can be utilized for exploration of the individual components of multicomponent systems.⁸ This incoherent elastic scattering technique is able to identify the formation of any solid monolayer over a wide temperature range much more quickly than diffraction.

DSC. The DSC measurements were performed on two Perkin-Elmer DSC7 power compensation method systems at the Polymers and Colloids Group, Cavendish Laboratory and at the Department of Materials Science and Metallurgy, both at the University of Cambridge. In these devices the sample and an empty reference can are heated at the same rate. The energy changes of any endothermic or exothermic transitions in the sample are compensated by providing more or less heating. The difference in electrical energy required to maintain the desired heating rate is a direct measure of the heat capacity of the sample. There are several advantages of this method including the absence of a temperature difference between the sample and reference, which would require a number of corrections. The optimum heating rate used was 10 $^{\circ}\text{C}/\text{min}$ and is a compromise between a slow rate, with good temperature precision, and a faster rate, which gives a more accurate magnitude of the energy changes, which appear as watts or joules per second. A slow rate of heating spreads the energy of a transition over a longer time, so the energy per unit time is small. The apparatus in the Polymers and Colloids group at the Cavendish Laboratory could go down to a minimum temperature of -65°C . The device at the Department of Materials Science and Metallurgy has a liquid nitrogen facility that allows measurements down to a temperature of -130°C .

Samples. The adsorbent used in these experiments was recompressed exfoliated graphite, Papyex (Le Carbone Lorraine), with a specific surface area of $14 \text{ m}^2 \text{ g}^{-1}$ determined by

TABLE 1: Quantities of Adsorbate and Graphite Used to Prepare Samples for DSC and INS Experiments^a

	alkane (mmol)	graphite (g)	area per molecule (\AA^2)
DSC Samples			
octane	0.78	1.23	52.4
nonane	0.19	0.58	57.6
decane	0.70	1.32	62.9
dodecane	0.37	0.75	73.3
INS Samples			
pentane	6.04	7.28	36.7
hexane	5.81	7.01	41.9
octane	5.97	8.90	52.4
nonane	1.15	4.10	57.6
decane	1.03	3.96	62.9

^a The estimates of the area per molecule on the basis of the model of Groszek are also given.

adsorption of nitrogen. Protonated alkanes were obtained from Aldrich and purified by passage through an alumina column (Brockmann I, activated, basic). Deuterated nonane, decane, and dodecane were obtained from Cambridge Isotope Laboratories and deuterated octane from Aldrich, all with a quoted deuteration level of $>99\%$. The graphite substrates were outgassed under vacuum in an oven before known quantities of the adsorbates were added as solid or liquid and annealed at a temperature just below the boiling point. For the DSC measurements approximately 20 mg of graphite was used dosed with fully protonated materials. When estimating the amount of adsorbate to add to the substrate, we have used estimates of the surface area per molecule¹³ and the specific surface area of the particular sample of graphite ($14 \text{ m}^2/\text{g}$). In this manner we can prepare samples with coverages in terms of a number of equivalent monolayers. From now on we refer to equivalent monolayers as monolayers, but, in each case, the true quantities of adsorbates and graphite used to prepare samples are given in Table 1.

Results

A. Differential Scanning Calorimetry. A.1. Pure Alkanes. The differential scanning calorimetry traces for (a) 15 monolayers of octane and (b) 15 monolayers of dodecane adsorbed on graphite are shown in Figure 1. The graphs are plotted such that an upward peak corresponds to an endothermic transition. Over the temperature range investigated here there are no features in the DSC trace for graphite alone. For octane, Figure 1a, the graph has two peaks. The lower temperature peak is at a temperature close to the bulk melting point of pure octane in the absence of graphite. The second peak, at temperatures above the bulk melting point, is not present either in the DSC trace of pure octane in the absence of graphite or in that of graphite alone. This peak must therefore arise from the interaction of the octane with the graphite surface, and the simplest conclusion is that it is a transition of an adsorbed layer. Nonane and decane, not shown, both show similar single peaks above the bulk melting transition corresponding to transitions in adsorbed layers. The DSC trace from dodecane, Figure 1b, shows the major transition at the bulk melting point and two transitions in the adsorbed layer region. Repeated measurements with several samples showed that the appearance of these two peaks was completely reproducible. The temperatures and enthalpies of the monolayer transitions are given in Table 2. For a first-order bulk melting transition the best estimate of the transition temperature in a DSC trace is the "on-set" value, while for a higher order transition, which may be expected for monolayer melting, the peak maximum position is more appropriate. Thus,

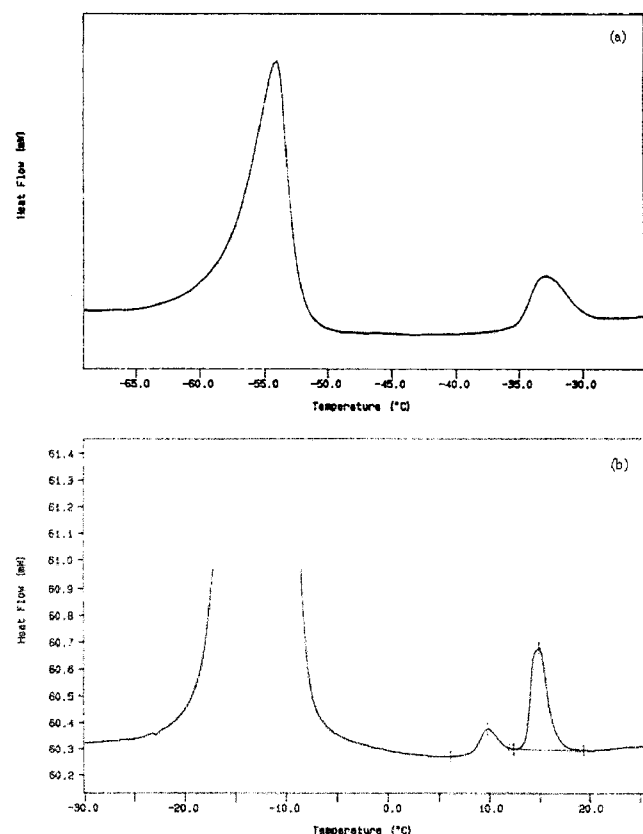


Figure 1. DSC traces of (a) 15 monolayers of octane and (b) 15 monolayers of dodecane adsorbed on graphite. Upward peaks correspond to endothermic transitions.

TABLE 2: Temperatures and Enthalpies of Transitions of the Bulk and Monolayer of Pure Alkanes at a Coverage of Approximately 14 Monolayers^a

alkane	T_{2D} (K) INS	T_{2D} (K) DSC	T_{3D} (K) DSC	T_{3D}^{lit} (K)	ΔH_{2D} (J/g graphite)
pentane				143.3	
hexane	198			177.7	
heptane	203 ^b			182.4	
octane	240	240	215	216.2	0.501
nonane	253	244.8	215	219.5	0.279
decane	265	264	239	243.3	0.387
dodecane	285 ^b	283, 288	256	263.4	0.052, 0.203

^a T_{2D} monolayer transition temperature, T_{3D} "bulk" transition temperature, T_{3D}^{lit} , literature value of bulk melting point, and ΔH_{2D} monolayer transition enthalpy. ^b Taken from ref 7.

the values of the transition temperatures given in Table 2 for the adsorbed layer and the bulk transition temperatures are peak maximum and on-set values, respectively. The uncertainty in the transition temperatures determined by DSC arises from the temperature scale calibration of the instrument, using indium, and the extrapolation procedures used to find the onset temperature. We estimate the combined error to be less than 2 °C.

Since the enthalpies of the adsorbed layer transitions given in Table 2 will be proportional to the overall surface area of the sample, the enthalpy values are given per gram of graphite. This makes them independent of any assumptions concerning areas per molecule on the surface, which would be a necessary input into any calculation of the enthalpy per gram or mole of adsorbate.

Figure 2 illustrates the evolution of the bulk and adsorbed layer transition temperatures with increasing coverage for octane. Although there is some evidence of a coverage dependence at

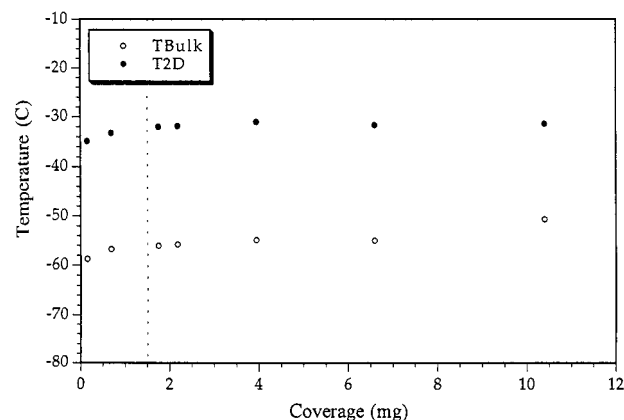


Figure 2. Coverage dependence of the bulk and monolayer transitions in DSC measurements for octane. The dotted line indicates approximately 10 monolayers coverage.

low coverages, it is evident that only a few monolayers are required before there is little further variation. Similar behavior has been reported for adsorbed inert gases on graphite where the coverage dependence of a transition that moved, increasing to the bulk melting point, was attributed to surface melting.

In the measurements reported here, where only a small sample of graphite was dosed with adsorbate, there is some uncertainty in determining the absolute coverage, particularly at submonolayer coverages. However, a series of experiments where larger quantities of graphite were dosed at a much lower relative coverage than shown in Figure 2 indicated a transition below the bulk melting point of the alkane in the submonolayer region. The temperature of this transition does not correspond to any transition of the bulk material, suggesting it is a transition of an adsorbed layer at coverages well below a monolayer. This transition moves to higher temperatures with increasing coverages, crossing the bulk melting point at a coverage corresponding approximately to a monolayer. This result is not unexpected, since there are many examples of adsorbed monolayers at submonolayer coverage that melt below their bulk melting point.⁶

Figure 3a shows the DSC trace for a mixture of approximately 15 monolayers of octane and 7 monolayers of dodecane. At the lowest temperatures the melting of octane is observed followed by the solubilization (the two liquids are known to be completely miscible in the bulk) of most of the dodecane. At higher temperatures, even though all the bulk material would be liquid and no further transitions are expected, there is still a transition, which we assign to a transition in the adsorbed layer. Figure 3b illustrates the temperature variation of the bulk and monolayer transitions over a range of compositions of octane/dodecane mixtures adsorbed onto graphite. The behavior of the bulk melting points is as expected and observed in the absence of graphite, i.e., it is depressed by increasing solute concentration. Figure 3b indicates that the adsorbed monolayer transition also follows this trend, remaining at a temperature approximately 1.1 times the bulk melting temperature of the solution. The two monolayer peaks of dodecane that are observed in the pure dodecane system ($x_{oct} = 0.0$) are seen to merge in the mixture as the octane concentration is increased to form a single peak. It is important to note that the DSC method is unable to distinguish which component or mixture of components is adsorbed at any composition and therefore to give any indication as to the mechanism of this change.

Similar composition dependence was observed with DSC measurements on binary mixtures of octane/nonane and octane/decane. With octane/nonane, where the bulk melting points are

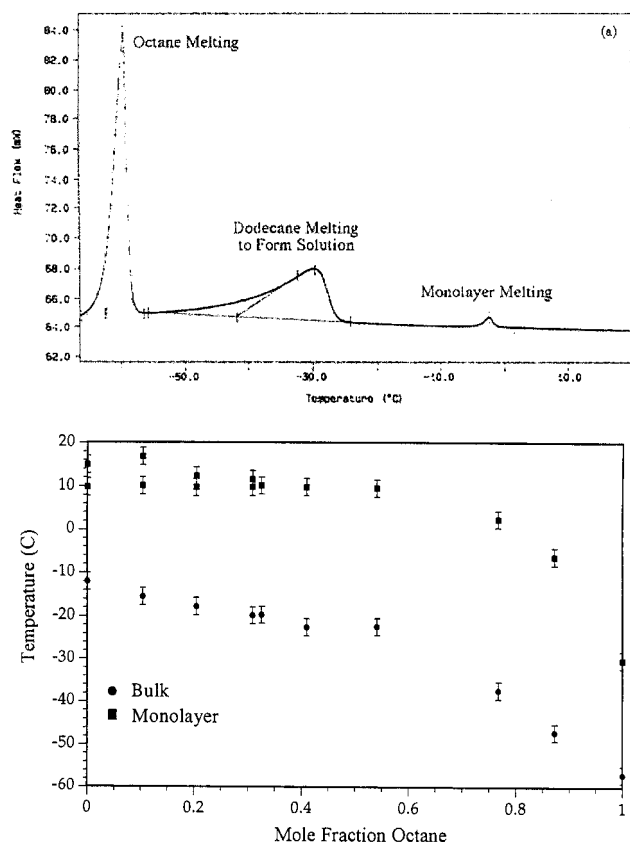


Figure 3. (a) DSC trace from a binary mixture of octane and dodecane at a mole fraction of $x_{\text{oct}} = 0.87$. (b) Composition dependence of the DSC transitions of octane/dodecane.

similar, only one bulk transition was observed corresponding to the combined melting with a slight depression of freezing point. In both systems the transition in the adsorbed layer was observed as in all the systems so far investigated

B. Incoherent Elastic Neutron Scattering. *B.1. Pure Alkanes.* Figure 4 shows the intensity of the incoherent elastic peak as a function of temperature for (a) 15 monolayers of h-pentane, (b) 15 monolayers of h-hexane, (c) 15 monolayers of h-octane, (d) 7 monolayers of h-nonane, and (e) 7 monolayers of h-decane. Similar data for methane, heptane, and dodecane have been presented elsewhere.⁷ The quantities of adsorbate and graphite are given in Table 1.

Parts b–e of Figure 4 all show similar behavior. At the lowest temperatures the alkanes are solid, giving a strong elastic signal. As the bulk melting points are approached and crossed, the intensity falls significantly. However, above the bulk melting temperatures there is still a significant residual intensity. At this temperature this residual intensity cannot arise from bulk solid material and must therefore result from the presence of immobile adsorbed species. We have discussed the time scale of this immobility in the previous papers.^{7,8} For the purposes of our discussion here, it means solidlike material. The residual intensity from the solid adsorbed layer is maintained to higher temperatures when the adsorbed layers melt and the elastic scattering falls to the level of the graphite background. The melting temperatures of the adsorbed layers can be estimated from these figures on the basis of the position of the end of the monolayer plateau and are given in Table 2. Because there is some uncertainty in the absolute temperature of the sample, we have taken the melting points of the bulk material as an internal reference and adjusted the temperature scale such that the experimentally measured bulk melting points agree with the

literature values. The uncertainty in this procedure leads to an error of approximately 3 °C in the monolayer transition temperatures. Even with this error, it is clear that the monolayer transition temperatures are in good agreement with the DSC measurements. The INS results confirm that the transitions observed in the DSC are associated with melting of the adsorbed layers. With the INS data a pronounced “odd–even” variation in the adsorbed layer melting point can be observed.

Pentane does not show the same features as the other alkanes but only exhibits a single drop in intensity at the bulk melting point. The intensity above the bulk melting point does not show the step characteristic of the melting transition of an adsorbed layer. If a solid adsorbed layer of pentane is present at the graphite surface, it must melt within approximately 5 K of the bulk melting point.

The intensity of elastic scattering just above the bulk melting points is proportional to the amount of material in the adsorbed layers.^{7,8} The elastic scattering intensity corresponding to one monolayer can be estimated using the total quantity of adsorbate in the sample cell, the elastic scattering intensity at low temperatures where all the adsorbate is solid, the specific surface area of the graphite (14 m²/g), and the area per molecule.¹³ These estimates are marked in Figure 4 and agree well with the observed intensity of scattering from the adsorbed layers. This simple calculation suggests that there is only a single layer adsorbed on the graphite and that the molecules are predominantly lying with their long axes parallel to the graphite surface, since Groszek’s estimate of the area per molecule was based on this molecular orientation.

B.2. Binary Mixtures of Alkanes. Mixtures of octane/nonane, octane/decane, and octane/dodecane were investigated with approximately 7 monolayers of nonane, decane and dodecane as “solvent” and 14 monolayers of octane as “solute”. As discussed above, the contributions from protonated components will dominate the incoherent scattering; the contribution from the deuterated components will always be relatively small. To examine the separate components of each mixture combinations of protonated and deuterated molecules such as, for example, a mixture of d-octane, C₈D₁₈, with h-nonane, C₉H₂₀ (scattering predominantly from the nonane), h-octane, C₈H₁₈, with d-nonane, C₉D₂₀ (scattering predominantly from the octane). By this means the amount of solid octane and nonane at each temperature could be determined separately. Similar protonated and deuterated combinations of octane and decane and octane and dodecane were used.

The actual contribution to the incoherent elastic scattering from each component depends on the incoherent cross section of the individual molecules. The actual protonated samples used in this work are taken to be fully protonated. However, the level of deuteration is important because even a small amount of protonated material will greatly increase the incoherent scattering from that component. Table 3 gives the incoherent scattering cross sections from the protonated and deuterated alkanes used in this work, and this takes into account the true extent of deuteration. The contribution of the deuterated component to the scattering can then be calculated for each of the alkane mixtures used. The mixtures consist of approximately 7 monolayers of solute and 15 monolayers of solvent (octane). Where the solute is deuterated it is estimated to account for approximately only 3% of the total scattering. Similarly, the contribution from d-octane as solvent is approximately 10% of the total scattering.

Figure 5 gives the incoherent elastic scattering intensity for mixtures of (a) 7 monolayers of h-dodecane and 15 monolayers

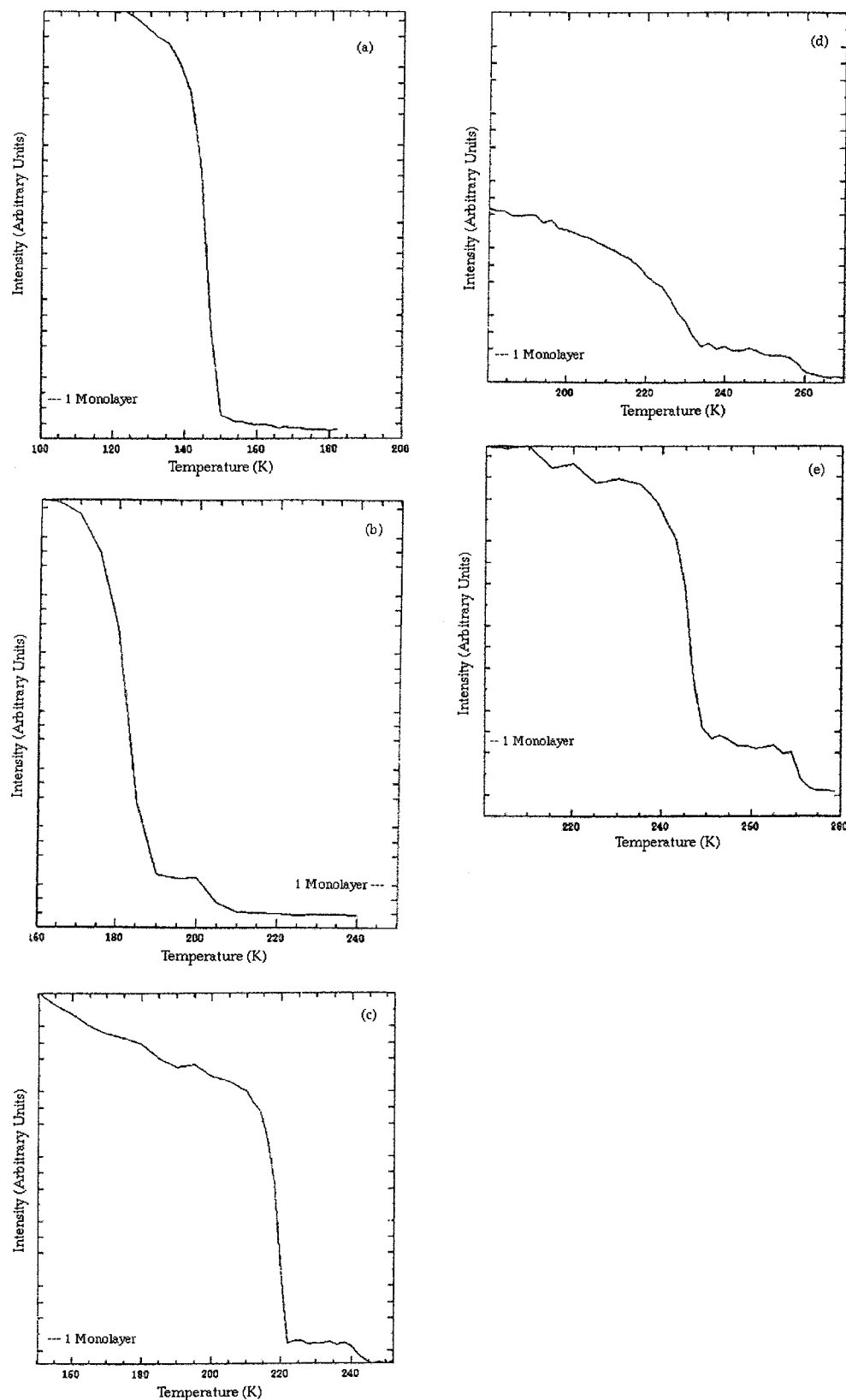


Figure 4. Incoherent elastic scattering as a function of temperature for (a) 15 monolayers of h-pentane, (b) 15 monolayers of h-hexane, (c) 15 monolayers of h-octane, (d) 7 monolayers of h-nonane, and (e) 7 monolayers of h-decane.

of d-octane and (b) 7 monolayers of d-dodecane and 15 monolayers of h-octane. Figure 6 shows (a) 7 monolayers of h-nonane and 15 monolayers of d-octane and (b) 7 monolayers of d-nonane and 15 monolayers of h-octane. As described above, the scattering in these figures is predominantly from the protonated components, i.e., Figure 5a is predominately from

dodecane, Figure 5b from octane, Figure 6a from nonane, and Figure 6b from octane.

The scattering from the alkane mixtures where the longer alkane is protonated, Figures 5a and 6a, exhibits features similar to those of the pure alkanes. Thus, in Figure 5a all the material is solid at low temperatures and, although deuterated, there is

TABLE 3: Incoherent Cross Sections for the Materials Used in This Work

molecule	incoherent cross section (Barns) protonated material	incoherent cross section (Barns) deuterated material
pentane	959	
hexane	1119	
heptane	1279	
octane	1438	64.76
nonane	1598	71.96
decane	1758	62.02
dodecane	2078	93.54

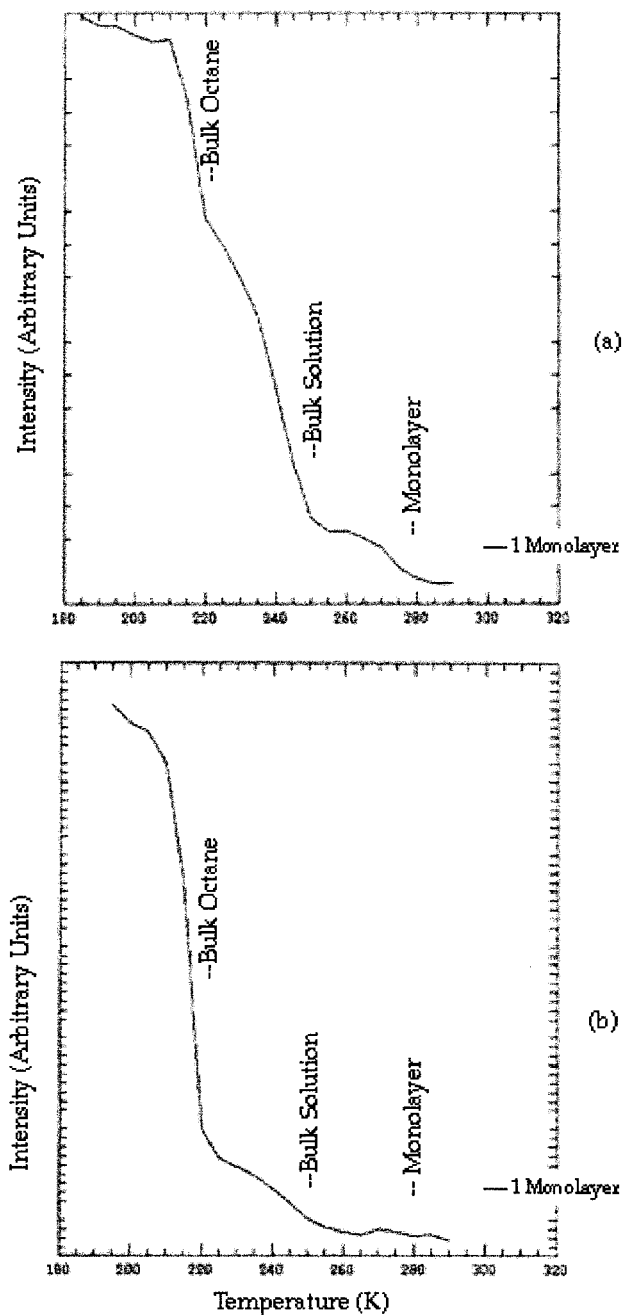


Figure 5. Incoherent elastic scattering as a function of temperature for (a) 7 monolayers of h-dodecane and 15 monolayers of d-octane and (b) 7 monolayers of d-dodecane and 15 monolayers of h-octane. These data were obtained at a momentum transfer, Q , of 1.416 \AA^{-1} , where Q is defined here as $(4\pi \sin \theta)/\lambda$ where λ is the neutron wavelength and θ is half the scattering angle.

a contribution from the octane melting indicated in the figure where the intensity of scattering does decrease. There is a

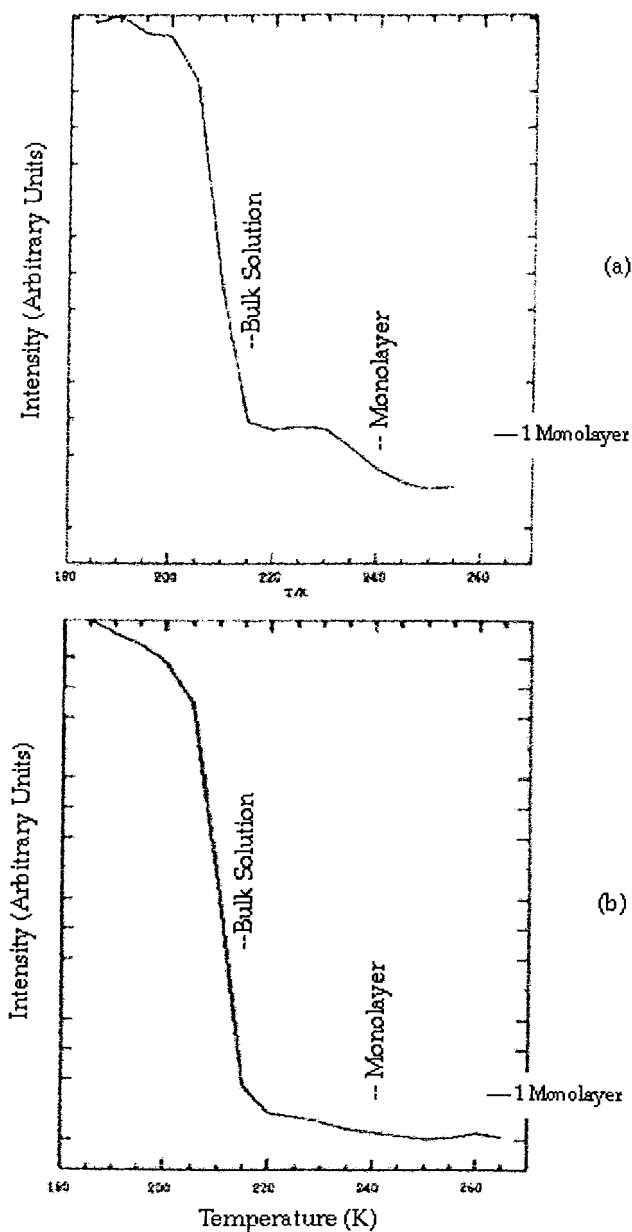


Figure 6. Incoherent elastic scattering as a function of temperature for (a) 7 monolayers of h-nonane and 15 monolayers of d-octane and (b) 7 monolayers of d-nonane and 15 monolayers of h-octane. The various transitions are discussed in the text. These data were obtained at a momentum transfer, Q , of 1.416 \AA^{-1} , where Q is defined here as $(4\pi \sin \theta)/\lambda$ where λ is the neutron wavelength and θ is half the scattering angle.

further, more pronounced, fall in intensity when the minority component, the dodecane, dissolves. Again, however, above the point where the bulk solution has formed, there is a residual intensity that we attribute to the presence of a solid adsorbed layer. This solid layer finally melts or dissolves, and the intensity falls to the background.

In Figure 5b the melting of the bulk octane is a much more significant feature as expected because it is now the protonated component. There is some residual scattering from dissolution of the deuterated dodecane, which arises from a combination of the incomplete deuteration and the intrinsic contribution from the deuteriums. However, it is clear that the monolayer evident in Figure 5a is no longer evident in Figure 5b. This demonstrates that, within the error of the measurement (about 10%), there is no solid octane adsorbed in the solid adsorbed layer. As earlier

shown in Figure 4, pure h-octane does form a solid monolayer. Thus, the longer alkane displaces octane from the surface.

Similar results are observed with the octane/nonane mixture illustrated in Figure 6. These data, and similar data for octane/decane, which are not shown here, again indicate that the longer alkane is preferentially adsorbed and forms the solid adsorbed layer. This is the case even for mixtures of octane and nonane, and even when octane is present as the major component in the mixture. The bulk melting points of octane and nonane are similar, so they melt together in one transition, unlike mixtures of octane and dodecane (and octane and decane).

Both bulk and adsorbed layer transition temperatures are shifted from the values of the pure alkanes. The transition corresponding to the dissolution of the solute follows that in the absence of graphite and is in line with the usual depression of freezing point. Once again, the results are in excellent agreement with the DSC measurements, but they give the added information about the composition of the adsorbed layer and the nature of the transition.

Discussion and Conclusions

A. Pure Alkanes. The results from the incoherent elastic scattering and DSC experiments on pure alkanes presented here extend our earlier diffraction work^{6–8} and confirm the formation of solid monolayers adsorbed from liquid alkanes above the bulk melting point. The present work indicates that a single solid monolayer is formed above the bulk melting point for hexane, octane, nonane, and decane adsorbed onto graphite from their respective liquid phases. This parallels the behavior previously observed for methane, heptane, and dodecane.⁷ The magnitudes of the monolayer melting temperatures relative to the bulk are also similar, the ratio being approximately 1.1. The results given here are consistent with the trend of monolayer melting points of longer alkanes reported recently.¹⁴ These workers also reported the formation of more than one solid monolayer.

The DSC and INS results show good agreement in the temperatures of the bulk melting and monolayer melting transitions. The melting points of the monolayers show some initial variation with coverage, but there is little further variation with coverage over 5–10 monolayers. The DSC indicates two transitions in the monolayer region for dodecane, although we cannot identify the causes of them at present. There are a number of possible phases, including two-dimensional rotator phases or lattice liquids. Only a single broad transition is observed in the INS measurements. Neutron diffraction work is under way to investigate these transitions in the dodecane monolayer.

The enthalpies of the monolayer transitions at higher coverages are much smaller than the bulk enthalpy of fusion for all alkanes investigated here and fall with increasing chain length. The relation between melting of three-dimensional to two-dimensional melting of the same material is expected to be complex, and it would be too speculative to discuss further in the absence of detailed structural information. We hope to have this information in the near future.

The bulk transitions of the alkanes in the presence of the graphite at low coverages have a much lower total enthalpy than the bulk without graphite, even allowing for the loss of material to the adsorbed monolayer. The liquid bulk alkane might be expected to adsorb on the graphite. If this were the

case, the endothermic melting transition would be offset by the exothermic residual heat of adsorption, and this would reduce the measured enthalpy. When the coverage is increased, the increment in the enthalpy of the peak will recover to the bulk value.

B. Mixtures of Alkanes. The incoherent elastic neutron scattering measurements demonstrate the formation of solid monolayers adsorbed from solution. They also show that the longer alkane is preferentially adsorbed even when present as the minor component in the mixture and even if it is only one CH₂ unit longer than the solvent. Over the concentrations studied, which for practical reasons did not include any extreme dilutions, the longer alkane is always adsorbed with the complete exclusion of the other within an experimental error of about 10%. The temperatures of the transitions were found to be in good agreement with the transitions observed in the DSC measurements.

The results presented here support the formation of monolayers with molecules lying with their long axis parallel to the surface. A recent STM study⁵ of heptacosane (C₂₇) has identified lamellar structures with extended carbon chains oriented parallel to the graphite basal plane, in good agreement with our results. X-ray diffraction studies of longer alkanes than studied here¹⁵ also concluded that these alkanes lie flat on the surface.

The presence of solid layers that melt above the bulk melting point has also been described in other multilayer systems such as neon and argon on graphite,¹⁶ referred to as “presolidification” and “substrate-induced freezing”. Some particular systems have also been reported to exhibit structural transitions. The number of solid layers is reported to depend on the total coverage such that solid bi-, tri-, and multilayers are formed. This is in contrast to the behavior of the adsorbed alkanes reported here for which there is only evidence for a single solid layer coexisting with the bulk liquid.

Acknowledgment. The authors thank U.K. EPSRC (S.M.C.), The Spanish DGICYT, and a Grant-in-aid for Scientific Research from Monbusho (A.I.) for financial support.

References and Notes

- (1) Findenegg, G. H. *J. Chem. Soc., Faraday Trans. 1* **1972**, 68, 1799.
- (2) Findenegg, G. H. *J. Chem. Soc., Faraday Trans. 1* **1973**, 69, 1069.
- (3) Kern, H.; Findenegg, G. H. *J. Colloid Interface Sci.* **1980**, 75, 346.
- (4) Fragneto, G.; Thomas, R. K.; Rennie, A. R.; Penfold, J. *Langmuir* **1996**, 12, 6036.
- (5) Rabe, J. P.; Buchholz, S. *Science* **1991**, 253, 424.
- (6) Clarke, S. M. D.Phil. Thesis, University of Oxford, 1986.
- (7) Castro, M. A.; Clarke, S. M.; Inaba, A.; Thomas, R. K. *J. Phys. Chem.* **1997**, B101, 8878–8882.
- (8) Castro, M. A.; Clarke, S. M.; Inaba, A.; Dong, C. C.; Thomas, R. K. *J. Phys. Chem.* **1998**, B102, 777–781.
- (9) Bee, M. *Quasielastic Neutron Scattering*; Adam Hilger, 1988.
- (10) Neutron Research Facilities at the ILL High Flux Reactor, Institut Laue-Langevin, Grenoble, France.
- (11) Coulomb, J.-P.; Bienfait, M.; Thorel, P. *Faraday Discuss. Chem. Soc.* **1985**, 80, 79.
- (12) Coulomb, J.-P.; Bienfait, M.; Thorel, P. *J. Phys.* **1981**, 42, 293.
- (13) Groszek, A. J. *Proc. R. Soc. London* **1970**, A314, 473.
- (14) Epeau, P.; White, J. J. *J. Chem. Soc., Faraday Trans.* **1997**, 93, 3197–3200.
- (15) Epeau, P.; Reynolds, P. A.; Dowling, T.; Cookson, D.; White, J. *J. Chem. Soc., Faraday Trans.* **1997**, 93, 3201–3208.
- (16) Hess, G. B. In *Phase Transitions in Surface Films 2*; Taub, H., Torzo, G., Lauter, H. J., Fain, S. C., Jr., Eds.; NATO ASI Series 267; Plenum Press: New York, 1991.