

Preferential Adsorption from Binary Mixtures of Short Chain *n*-Alkanes; The Octane–Decane System

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The competitive adsorption of the alkanes *n*-octane and *n*-decane adsorbed from the binary liquid mixture onto graphite has been studied using differential scanning calorimetry (DSC), neutron diffraction, and incoherent quasi-elastic neutron Scattering (IQNS). A solid monolayer is identified at all bulk solution compositions with a melting temperature that varies with bulk composition in a manner resembling the bulk behavior. The IQNS data indicates that decane is preferentially adsorbed onto the surface over most of the composition range, as expected. However, octane can coexist on the surface with decane and even becomes the principal component at high octane concentrations. When both alkanes are present on the surface, diffraction indicates that the surface phase is not a mixed crystal, but consists of regions of pure octane and regions of pure decane. The failure of these two compounds to mix on the surface is shown to have its origin in the structures of the monolayers of the pure components.

Introduction

Adsorbed monolayers in contact with liquid play an important role in many interfacial phenomena, such as lubrication and detergency. However the presence of the bulk liquid creates a buried interface that makes it difficult to obtain structural information about the layers. As a result there is only limited elementary information about layers adsorbed at the solid/liquid interface. Recent work on alkanes adsorbed onto a graphite surface from their liquids using neutron scattering techniques and differential scanning calorimetry has revealed that many alkanes form a solid surface layer coexisting with the bulk liquid.^{1–6} This surface layer (one molecule thick) has a melting point approximately 10% higher than the bulk, and the molecules are found to lie with the axis of the carbon backbone parallel to the surface.

Most systems of practical value involve adsorption from multicomponent liquid mixtures⁷ either because mixtures are cheaper than pure components or because of some synergy between components of the mixture. These more complex systems will evidently be even more difficult to study than adsorption from a single pure liquid. Previous experimental work on binary alkane mixtures has shown that when one alkane is significantly longer than the other, only the longer molecule is adsorbed onto graphite to any meaningful extent.^{1,4} Interestingly, recent computer simulations on butane and octane mixtures

adsorbed on graphite have reported the opposite behavior.⁸ When the alkanes are of similar lengths then both species can compete effectively for the surface and can even coexist on the surface. Under such conditions the mixing behavior on the surface is important. Mixing behavior in the bulk alkanes is complex but it is generally found that alkanes similar in length with the same space group can form mixed crystals. Hence in this work we have investigated mixed monolayers of octane and decane where the molecules are similar in alkyl chain length and, as shown below, the monolayers of the pure components have the same plane group, so mixing might be expected in the monolayer.

In this work we present data from a combination of techniques that can provide detailed structural and compositional information on the binary mixture of the alkanes octane and decane. Differential scanning calorimetry is used to map the phase behavior with bulk solution composition, but is limited by the fact that it cannot identify the composition of the monolayer. For this we have used IQNS measurements, followed by diffraction measurements to identify the structural characteristics of the pure and mixed monolayers.

Experimental Section

Sample Preparation. The graphite substrate used in these experiments was Papyex, a commercial material supplied by Le Carbone Lorraine. The specific surface area, determined by adsorption of nitrogen, was found to be between 12 and 25 m²/

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TABLE 1: Incoherent Scattering Cross-Sections of the Molecules Used in This Work

molecule	theoretical incoherent cross-section (barns)	
	protonated	deuterated
octane	1438	65
decane	1758	62

g. Small disks of approximately 5 mm in diameter and mass of 0.2 g were used in the DSC experiments. For the neutron experiments stacks of rings of graphite were used instead to minimize transmission problems while optimizing the quantity of sample in the beam. Typically, 7 g was used for the IQNS and 12 g for the diffraction measurements. The samples were cleaned at 350–400 °C under vacuum before dosing, in situ and under helium, with the required amount of liquid adsorbate. The amount required for a particular coverage was estimated from the area per molecule (using the Groszek model⁹) and the specific surface area of the Papyex determined by nitrogen adsorption. In the DSC measurements a large excess (15 μ L) of the appropriate composition alkane mixture was added to give an excess corresponding to 90 monolayers. This excess is referred to as “bulk” to distinguish it from the adsorbed material. In the neutron experiments the amount of bulk adsorbate was kept as small as possible to minimize its scattering contribution relative to that from the adsorbed layer. In all cases the samples were annealed at elevated temperature.

Differential Scanning Calorimetry (DSC). The DSC technique and its application to the study of adsorbed layers have been described elsewhere.^{2,10} In brief, the small changes in heat capacity from an adsorbed monolayer transition can be observed with sensitive DSC despite the presence of significant quantities of bulk material. These monolayer transitions include melting as well as other solid–solid transitions. The transitions appear as peaks in the heat flow with an area proportional to the enthalpy change for that transition. The contribution from the adsorbed monolayer is optimized by the use of powdered substrates with a high specific surface area and a very homogeneous surface. The measurements were made on a Perkin-Elmer Pyris 1 series, power compensation method calorimeter. The scan rate was typically 10°/min, representing a compromise between sensitivity and temperature resolution.

Incoherent Quasi-Elastic Neutron Scattering (IQNS). The IQNS technique and its application to the study of adsorbed layers have been described elsewhere.^{2,10} In brief, the intensity of elastic scattering is proportional to the quantity of solidlike, translationally invariant material in the sample. Because protons are much more strongly scattering than any other nucleus, even than deuterium, we can selectively investigate those components of the system that are protonated when the remainder are deuterated. This provides the means to investigate the adsorption of multicomponent mixtures. Scattering from the mobile fluid phases is quasi-elastically broadened and, for these materials, will provide no significant elastically scattered intensity when measured on an instrument with good energy resolution.

The high-energy resolution required to measure the elastically scattered neutrons was achieved using the high-resolution backscattering instrument IN10 at the Institute Laue-Langevin, Grenoble, France.¹¹ The resolution is approximately 1 μ eV (fwhm). Unfortunately there is always a small contribution from the deuterated alkanes because of the small intrinsic incoherent scattering from deuterium but also because components are never completely deuterated, and as little as 1% hydrogen is enough to have a significant signal. The incoherent scattering cross-sections for the materials used in this study are given in Table 1.

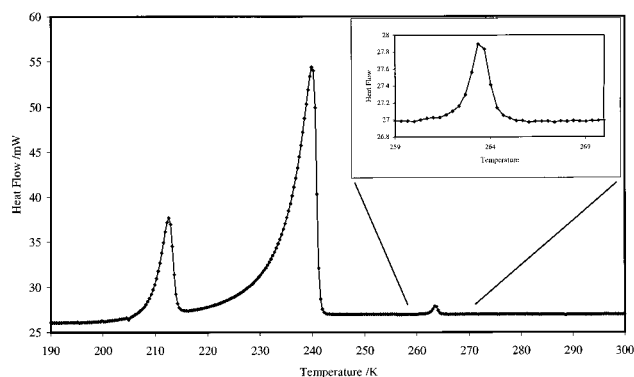


Figure 1. DSC thermogram for a mixture of octane and decane at a mole fraction, X_{oct} , of 0.75 adsorbed on graphite. The two large peaks at low temperature are identified as arising from transitions in the bulk. The weaker feature at the higher temperature of -10 °C, 263 K, is ascribed to a transition in an adsorbed monolayer. The inset in Figure 1 shows a magnification of this monolayer region.

Neutron Diffraction. The use of neutron diffraction for the study of adsorbed binary mixtures has been described elsewhere.^{2,3} The experiments were conducted on D1B and D20 at the Institute Laue Langevin, Grenoble, France, and on OSIRIS at the Rutherford Appleton Laboratory, Oxfordshire. The measurements on D1B and D20 provide diffraction data across a wide enough Q -range for the determination of the crystallographic structures for adsorbed layers of the pure alkanes. The high-resolution patterns from OSIRIS are collected over narrower Q -ranges but the higher resolution allows the separation of closely spaced peaks permitting the phase behavior of the binary mixtures to be determined. Deuterated molecules were used to minimize the incoherent scattering that would have arisen with protonated species.

Results

A typical DSC thermogram is shown in Figure 1 for a mixture of octane and decane at a mole fraction, X_{oct} , of 0.75. The bulk phase behavior including the eutectic invariant (-60 °C, 213 K) and melting (-33 °C, 240 K) are easily identified by comparison with the DSC traces given in.¹² Significantly, at the higher temperature of -10 °C, 263 K, another much smaller peak is observed which is not present in either the pure alkane mixture in the absence of graphite or for the bare graphite. We ascribe this feature to a transition in an adsorbed monolayer, as discussed previously.¹⁰ The inset in Figure 1 shows a magnification of this region.

Figure 2 shows the phase diagram for the octane/decane system in the presence of graphite as a function of solution composition determined from the DSC measurements. Drawn over this experimental data is a schematic illustration of the bulk phase behavior in the absence of graphite.¹² The bulk mixture shows classic eutectic behavior in which the components do not mix in the solid phase, except for compositions at the extremes of the phase diagram. The eutectic point is found at a mole fraction of decane (X_{C10}) of approximately 0.16 and at 212 K (-59 °C).

The monolayer melting transition also shows a distinctive composition dependence that appears to be similar to the bulk behavior, although the minimum is more pronounced and occurs at a slightly different composition ($X_{\text{C10}} = 0.12$). We note here that the composition axis for the monolayer melting cannot be known from the DSC because the surface composition is not necessarily the same as the bulk solution if there is preferential adsorption. We return to this point below. The form of the

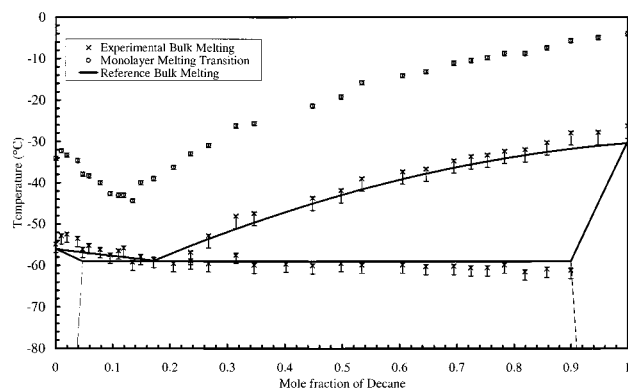


Figure 2. Phase diagram for the octane/decane system in the presence of graphite as a function of solution composition determined from the DSC measurements. Drawn over the experimental data points is a schematic illustration of the bulk phase behavior in the absence of graphite.¹²

temperature dependence of the monolayer indicates eutectic behavior, just as in the bulk. However, the low signal from the monolayer seems to make it impossible to observe the enthalpy change at the eutectically invariant temperature. The composition dependence of the enthalpy is essentially linear across the phase diagram with no depression at intermediate compositions. As discussed by ref 12, such a linear relationship is also indicative of eutectic behavior.

Figure 3a shows the IQNS data as a function of temperature for a range of solution compositions. The data represented by the topmost line are for pure h-octane. As reported previously this temperature variation has the form expected for a material where there is solid monolayer formation above the bulk melting point.¹⁰ At low temperatures all the adsorbate is solid, whether adsorbed on the surface or not, and the elastic intensity is high. On passing the bulk melting point the intensity falls as the bulk adsorbate melts. However, the intensity does not fall to zero but only to a residual intensity proportional to the amount of solid decane in the adsorbed layer. At even higher temperatures this solid monolayer also melts and the scattering falls to background. The temperatures of the transitions were found to be in reasonable agreement with those observed by DSC.

The relative intensity level expected for a monolayer of octane molecules lying with their carbon chains parallel to the surface can be estimated. Dividing the specific surface area of the graphite by an estimate of the area per molecule (based on Groszeks model) the number of molecules on the surface can be obtained as a fraction of the total adsorbate present. The intensity of scattering from all the adsorbate is obtained at low temperatures where all the adsorbate is solid. Thus the level of scattering from a solid monolayer can be estimated. This level is indicated in the figure by a horizontal dashed line and confirms that there is only a single monolayer involved and the molecules do indeed lie flat on the surface.

Two other compositions are also shown in the figure. These were made by successive additions of d-decane to the h-octane sample, to achieve the required composition. With this isotopic combination the elastic scattering is dominated by the protonated octane component. As the composition is changed it can be seen that the bulk melting moves to lower temperature and becomes broader, in good agreement with the DSC results and as expected from the continuous melting behavior of a eutectic system. The Figure also illustrates that the monolayer melting points are reduced with increasing decane, again in good agreement with the DSC data. However, there is a significant decrease in the level of the residual intensity corresponding to the solid

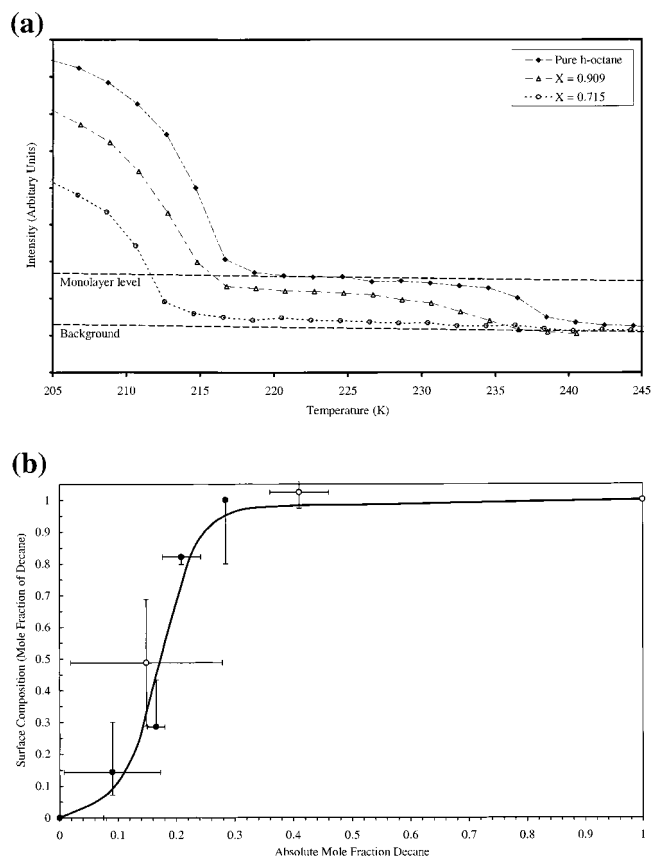


Figure 3. (a) IQNS data from octane/decane mixtures adsorbed on graphite as a function of temperature for a range of solution compositions. The bulk compositions correspond to (top) pure h-octane, (middle) $X_{\text{oct}} = 0.91$, and (bottom) $X_{\text{oct}} = 0.715$. The horizontal lines indicate the intensity levels of the background and that expected for a single molecular layer with the molecules lying flat on the surface. (b) Surface composition as a function of bulk solution composition deduced from Figure 3a (closed circles) and equivalent data from IQNS measurements on h-decane and d-octane (open circles).

monolayer clearly indicating that the amount of solid octane in the monolayer is falling on addition of decane. This result indicates that there is preferential adsorption of decane and provides a quantitative measure of the variation in surface composition with variation in bulk solution composition. The complete displacement of octane requires only small quantities of decane such that by a composition of $X_{\text{oct}} = 0.72$ ($X_{\text{dec}} = 0.28$) there is almost no h-octane on the surface. The relative composition of the surface layer can then be calculated by comparison of the level of the residual intensity for a given composition, with that of the pure alkane. The surface composition determined in this manner is shown in Figure 3b. The figure also presents data from the complementary h-decane/d-octane system (open circles), where the scattering is predominantly from the decane component (expressed as the amount of adsorbed octane from $X_{\text{oct}} = 1 - X_{\text{dec}}$).

In these IQNS experiments only small quantities of adsorbate are added and, because of the preferential adsorption, the composition of the bulk solution is slightly different from the original composition. However, once the monolayer composition is known appropriate corrections are readily made.

Crystal Structures of Pure Adsorbed Octane and Decane.

An important factor in understanding the surface mixing behavior is the monolayer structure of each of the pure components. Here we present neutron diffraction data from solid monolayers of pure octane and decane at both submonolayer

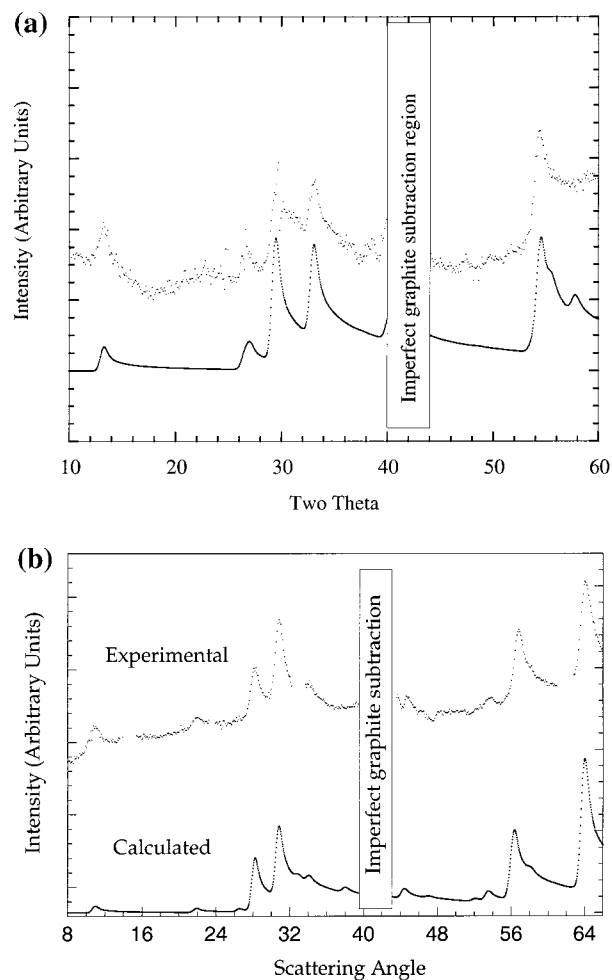


Figure 4. Experimental and calculated neutron diffraction patterns from submonolayer coverages of (a) octane and (b) decane adsorbed on graphite. The calculated patterns are based on the structures given in Figure 5 as discussed in the text. The region of imperfect graphite subtraction has been indicated in the figure.

and multilayer coverages. The crystal structures are found to be isomorphous with the shorter even alkane monolayers, butane and hexane.

Figure 4 shows the experimental neutron diffraction patterns from 0.8 monolayers of (a) octane and (b) decane adsorbed on graphite at 150 K. The intense scattering from the graphite background has been subtracted in preparing these patterns. Features arising from imperfect background subtraction are indicated in the figure and usually only arise when the graphite diffraction is strong. Fully deuterated alkanes were used to minimize the strong incoherent scattering characteristic of protonated materials. The solid lines in Figure 4, parts a and b, are calculated patterns based on the structures given in Figure 5, parts a and b, for octane and decane, respectively. These model structures, with cell parameters, $a = 21.13$ Å, $b = 5.35$ Å, and $\nu = 90$ for octane and $a = 25.5$ Å, $b = 5.4$ Å, and $\nu = 90$ for decane, are isomorphous with those reported for hexane and butane on graphite.^{6,13} The molecules have been taken to have identical bond lengths and bond angles as the bulk alkanes.¹⁴ The structures are uniaxially commensurate in the a -axis direction (53 by 5.35 Å for octane and $6\sqrt{3}$ by 5.4 Å for decane) with two molecules in the unit cells arranged with pgg symmetry and inclined at 30 degrees to the a -axis. In fitting the experimental data there is essentially only one variable, the length of the b -axis. Given the simplicity of the model the fit is remarkably good.

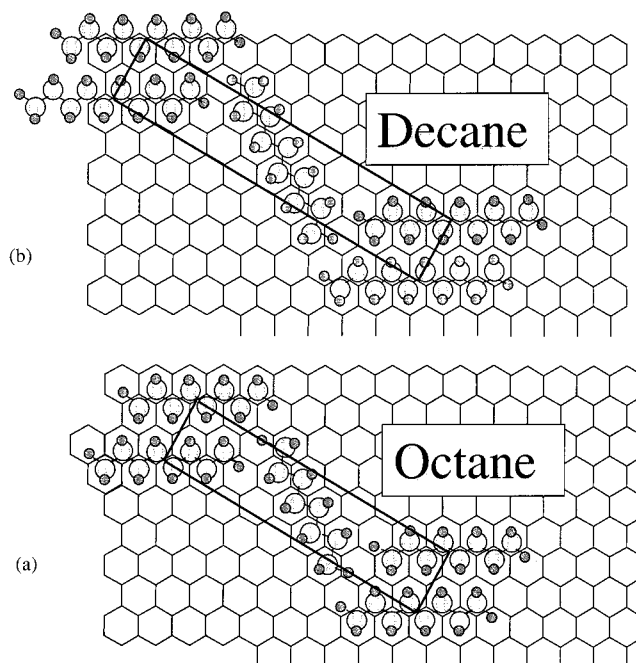


Figure 5. Schematic illustrations of the monolayer structures of (a) octane and (b) decane on graphite.

Figure 6 shows the experimental diffraction patterns from the solid monolayers of (a) octane and (b) decane adsorbed on graphite at 220 K and 260 K, respectively, at total coverage of 3 monolayers. The graphite pattern has been subtracted in preparing these patterns as described above. Additionally the scattering from liquid alkane has also been subtracted as described previously to obtain the scattering pattern from the solid adsorbed layers alone. The solid lines in Figure 6, parts a and b, are calculated patterns based on the structures given in Figure 5, parts a and b, for octane and decane, respectively. These structures, with cell parameters, $a = 21.3$ Å, $b = 4.92$ Å, and $\nu = 90$ for octane and $a = 25.4$ Å, $b = 5.2$ Å, and $\nu = 90$ for decane, are again isomorphous with those reported for high coverage hexane.⁶ The octane structure is now fully commensurate in both the a -axis and b -axis directions ($5\sqrt{3}$ by 2) with molecules arranged in symmetry inclined at 30 degrees to the a -axis. The decane structure has also undergone a uniaxial compression in the b -axis direction relative to the submonolayer coverage but, unlike octane, it is not quite fully commensurate in this direction ($6\sqrt{3}$ by 5.12 Å) (the discrepancy is outside the experimental error). Again in fitting all the experimental data there is essentially only one variable, the length of the b -axis.

The surface area per molecule for both octane and decane at high and low coverages can be calculated from these structures and are given in Table 2 together with values based on the model of Groszek.⁹ It is seen that the Groszek model is better at higher coverage for the fully commensurate octane layer. As the Groszek model was based on adsorption from solution and assumes a commensurate layer this behavior can be expected. The higher experimentally determined surface areas differ because of the uniaxial incommensurate nature of the layer. Other workers have also reported disagreements with Groszek's model for adsorbed alkanes on graphite.¹

The fact that the decane layer at high coverages is still uniaxially commensurate is significant. The carbon-carbon distance in the graphite surface and the alkane molecules is very similar and could favor commensurate overlayers. However, the match is not perfect and by decane there may be sufficient mis-

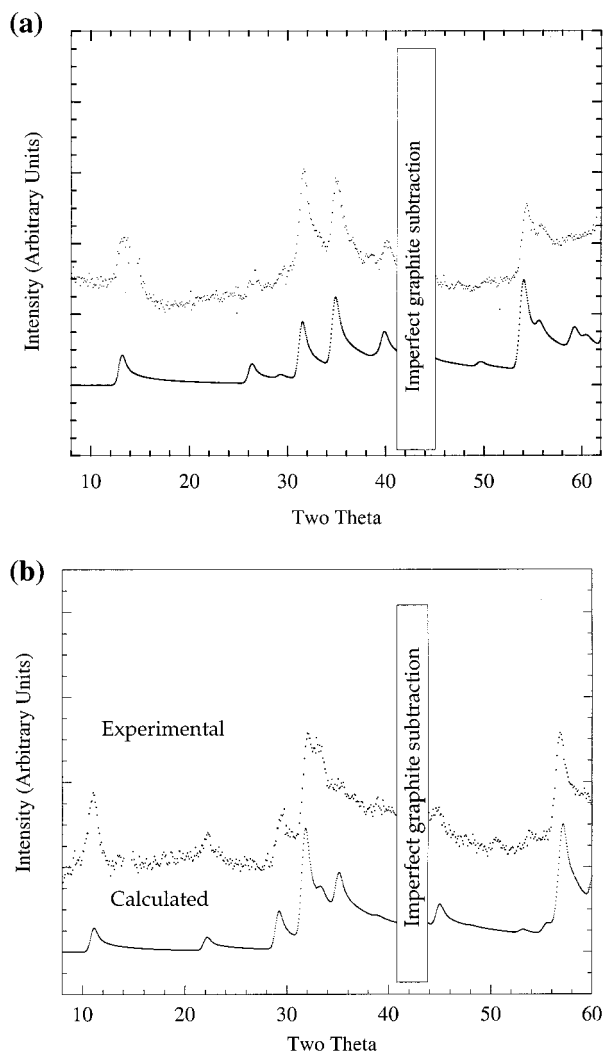


Figure 6. Experimental and calculated neutron diffraction patterns from high coverage structures of (a) octane and (b) decane adsorbed on graphite. The calculated patterns are discussed in the text.

TABLE 2: Comparison of the Area Per Molecule As Determined by IQNS, Neutron Diffraction, and the Groszek Estimate (All values are given in Å².)

	IQNS	neutron diffraction low coverage	neutron diffraction high coverage	Groszek
octane	56.5	56.5	52.4	51.5
decane	69.1	68.9	66.0	62.0

match to prevent a fully commensurate layer from forming. It has been reported that longer alkanes, odd and even, do not form the herringbone, *p*gg, molecular arrangement but lie parallel to each other.^{15,16} It appears that this may occur between decane and dodecane.

All four patterns, for octane and decane at low and high coverage, are fitted well by a simple isomorphous structure, which also works for hexane and butane monolayers. This provides some confidence in the structural solutions presented here, although it is important to note that these patterns are somewhat insensitive to the orientation of the carbon backbone on the graphite surface. Further work is under way to refine these structures with the inclusion of X-ray scattering data and data from other isotopically labeled molecules. The more detailed structures are not relevant to the present work that focused only on the mixing behavior.

Diffraction from Adsorbed Octane and Decane Mixtures. Neutron diffraction can be used to determine the mixing

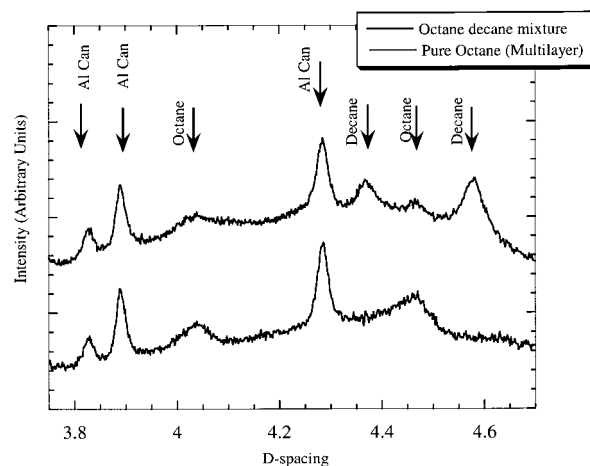


Figure 7. Neutron diffraction data from a mixture of octane and decane adsorbed on graphite at a composition where both are species present on the surface in equal amounts. The scattering pattern from pure octane at high coverages is shown for comparison. This pattern contains peaks from both pure octane and pure decane.

behavior of adsorbed layers, as described previously. In outline, when the adsorbed layer is phase separated the pattern consists of peaks that correspond to both pure components with intensities which depend on the amount of each pure component present. However, if the layer forms a mixed crystal then peaks from the two pure components will be replaced by new features.⁵

Figure 7 shows neutron diffraction data from a mixture of octane and decane adsorbed on graphite at such a composition (determined by IQNS) that both species are present on the surface in equal amounts, corresponding to a bulk solution composition of $X_{C10} = 0.1$. In Figure 7, the key features are the peaks from the adsorbed monolayers. The very broad scattering peak from the bulk, which is fluid at this temperature, only provides an additional background over the limited region of the scattering patterns shown here. The scattering pattern from pure octane at high coverages is shown for comparison. As indicated in Figure 7, this pattern contains peaks from both pure octane and pure decane clearly indicating that the octane and decane monolayers are separate phases. This is in excellent agreement with the calorimetry results.

Discussion and Conclusions

The combination of results from calorimetry, incoherent neutron scattering, and neutron diffraction data show that octane and decane do not mix on the surface of graphite. The behavior of the melting point and enthalpy of the surface melting transition also suggest a two-dimensional eutectic. The incoherent scattering data show that the longer of the two alkanes is preferentially adsorbed over most of the composition range, as expected, although octane competes effectively for the surface when present in the solution at some excess. Combining the composition information from the IQNS with the calorimetric data gives the surface eutectic diagram shown in Figure 8. This is much more symmetrical than implied in Figure 2. It is what would be expected when the entropy of mixing in the adsorbed liquid is symmetrical in composition and the enthalpies of fusion of the two monolayers are similar. For two molecules so similar in size and nature we would also expect the entropy of mixing of the two pure liquids to be close to the symmetrical ideal expression.

Eutectic behavior is also observed in the phase separation of octane and nonane, but in this case this can be attributed to the differences in space group of the pure solid monolayers.

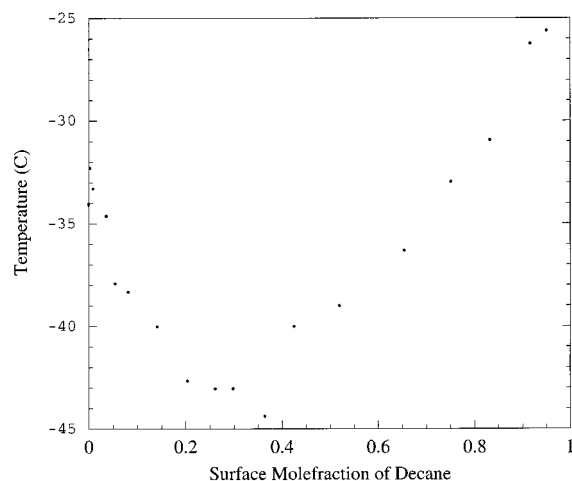


Figure 8. The monolayer phase diagram, in terms of the surface composition, estimated from the calorimetry and IQNS data given above.

However, we have demonstrated that octane and decane have the same space group. To explain this behavior we draw on results from the bulk alkane phase behavior where a coefficient of isomorphism ϵ_m^i can be defined which gives a quantitative measure of the similarity of the unit cells of two components of a mixture:¹²

$$\epsilon_m^i = 1 - \frac{\Delta_m}{\Gamma_m}$$

where Δ_m is the volume due to the nonoverlapping parts (when the two unit cells are positioned so as to achieve maximum overlap) and Γ_m is the volume due to the overlapping parts. When the value of ϵ_m^i for a pair of alkanes is approximately

0.88 or above, the two alkanes are found to be completely miscible in the solid phase. If this equation is applied to the two-dimensional situation, using unit cell areas instead of volumes, we find that in the case of octane/decane ϵ_m^i is only 0.80 and thus, based on this criteria, we would not expect octane and decane to mix on the surface at high coverages.

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References and Notes

- (1) Herwig, K. W.; Matthies, B.; Taub, H. *Phys. Rev. Lett.* **1995**, *75*, 3154–3157.
- (2) Castro, M. A.; Clarke, S. M.; Inaba, A.; Thomas, R. K. *J. Phys. Chem.* **1997**, *B101*, 8878–8882.
- (3) Castro, M. A.; Clarke, S. M.; Inaba, A.; Dong, C. C.; Thomas, R. K. *J. Phys. Chem.* **1998**, *B102*, 777–781.
- (4) Castro, M. A.; Clarke, S. M.; Inaba, A.; Arnold, T.; Thomas, R. K. *J. Phys. Chem.* **1998**, *B102*, 10528–10534.
- (5) Castro, M.; Clarke, S. M.; Inaba, A.; Arnold, T.; Thomas, R. K. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5017–5023.
- (6) Taub, H. In *The Time Domain in Surface and Structural Dynamics*; Long, G. J., Grandjean F., Eds.; Kluwer: Dordrecht, 1988; Vol. 228.
- (7) Gilbert, E. P.; Reynolds, P. A.; Thiyagarajan, P.; Wozniak, D. G.; White, J. W. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2715–2724.
- (8) Smith, P.; Lynden-Bell, R. M.; Smith, W. *Mol. Phys.* **2000**, *98*, 255–260.
- (9) Groszek, A. J. *Proc. R. Soc. London* **1970**, *A314*, 473.
- (10) Castro, M. A.; Clarke, S. M.; Inaba, A.; Thomas, R. K. *Physica B* **1998**, *241–243*, 1086–1088.
- (11) ILL, (Institut Laue-Langevin, Grenoble, France, 1996).
- (12) Rajabalee, F.; Espeau, P.; Haget, Y. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1995**, *269*, 165–173.
- (13) Herwig, K. W.; Newton, J. C.; Taub, H. *Phys. Rev. B* **1995**, *50*, 15287–15297.
- (14) Norman, N.; Mathisen, H. *Acta Chem. Scand.* **1961**, *15*, 1755.
- (15) Gilbert, E. P.; Reynolds, P. A.; White, J. W. *Colloids Surf., A* **1998**, *141*, 81–100.
- (16) Hansen, F. Y.; Herwig, K. W. *Phys. Rev. Lett.* **1999**, *83*, 2362–2365.