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Adsorption behaviour of the binary mixtures of octane and nonane at sub-monolayer coverage on graphite

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The behaviour of binary mixtures of octane and nonane adsorbed on graphite has been investigated with a combination of adiabatic calorimetry and neutron diffraction. In contrast to the eutectic behaviour of monolayers of these materials at higher coverages, this combination of alkanes is found to form mixed crystals on the surface over an extensive composition range at the sub-monolayer coverages investigated here. In the mixed phase the shorter octane molecules are incorporated into the lattice of the longer nonane molecules. This incorporation occurs despite pure octane and nonane monolayers having different symmetries and is attributed to the expanded nature of the submonolayer phases, relative to higher coverage monolayers, providing room for mixed crystal formation.

Introduction

Adsorption from liquids and solutions to solid surfaces is central to many academic and industrial problems, including lubrication, catalysis and detergency. Almost all industrial situations involve multicomponent mixtures, either because mixtures are cheaper than pure components or because the simultaneous adsorption of more than one component can lead to an enhanced behaviour relative to the pure components alone. However, obtaining detailed structural information or even determining the phase behaviour at the solid/solution interface is particularly difficult and, as a result, our understanding of these important adsorbed layers is still very limited.

Previous work in this area has focussed on adsorbed binary mixtures where one component is significantly longer than the other.[1–6] In such cases it is generally reported that the longer component is preferentially adsorbed to the complete exclusion of the other at any practical solution composition. However, recent computer simulation results have reported the opposite behaviour,[7] with the shorter alkane being preferentially adsorbed. Adsorption from solution has been reported to give rise to monolayer structures[1] that are different from those formed by adsorption from the vapour. However, the structural changes reported—uniaxial compression in the ***b***-axis—can also arise when the total coverage is increased.

To investigate the mixing behaviour of adsorbed binary solutions at the surface it is important to carefully control the alkyl chain lengths of the components and the composition of the bulk solution such that both components are co-adsorbed.[4,8] We recently reported the adsorption behaviour of octane and nonane mixtures adsorbed on graphite at high (greater than monolayer) coverages.[8] This work, combining calorimetry, incoherent and coherent neutron scattering, clearly indicated phase separation of the two components, that were simultaneously adsorbed in a solid monolayer that coexists with bulk solution. This phase separation arises because the two components have monolayers with different space groups.

Here we describe data from monolayers of octane and nonane at sub-monolayer (0.8) coverage using sensitive adiabatic calorimetry and coherent neutron diffraction that indicates that there is mixed solid monolayer formation over a wide composition range.

Experimental

Sample preparation

The graphite substrate used in these experiments was Papyex, a commercial material described previously,[9] and the specific surface area was determined by adsorption of nitrogen. For the adiabatic calorimetry measurements a stack of small discs of approximately 20 mm in diameter were used. For the neutron diffraction measurements a stack of graphite rings of external diameter 20 mm and internal diameter 8 mm with a total mass of approximately 12 g were used. Rings of graphite were used in the neutron experiments to minimise transmission problems but maximise the diffracted signal. The samples were cleaned at 350–400 °C under vacuum before dosing, *in situ*, with the required amount of liquid adsorbate. The amount required for a particular coverage was estimated from the area per molecule (using the Groszek model[3]) and the specific surface area of the Papyex. In the calorimetry measurements the total coverage was maintained at 0.8 of a monolayer. The diffraction measurements were made at total coverages of 0.8 and 5 monolayers. In all cases the samples were annealed at elevated temperature.

Adiabatic calorimetry

The method and experimental details of adiabatic calorimetry have been presented in detail elsewhere.[10] Essentially, the heat capacity of a sample of substrate (graphite) dosed with a known amount of adsorbate is directly determined as a function of temperature by adding tiny amounts of electrical heating energy to the sample and measuring the temperature rise. Transitions are indicated as peaks in the heat capacity.

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Neutron diffraction

The use of neutron diffraction to study adsorbed binary mixtures has been described elsewhere.[8,11,12] The experiments were conducted on OSIRIS at the Rutherford Appleton Laboratory, Oxfordshire, UK. This instrument has a variable incident wavelength and a single fixed detector bank such that almost all the counted neutrons are back-scattered. Used in this geometry OSIRIS has a high resolution that is required for these experiments.

Results

Adiabatic calorimetry

Fig. 1(a) presents the adiabatic calorimetry data from octane–nonane mixtures adsorbed on graphite at a total coverage of 0.8 monolayer at compositions of (mole fraction of octane, X_{oct}) 0, 0.217, 0.427, 0.626, 0.817 and 1.0. The equivalent area fractions, A_{oct}, are 0, 0.2, 0.4, 0.6, 0.8 and 1.0 respectively. The positions of the peaks in Fig. 1(a) are plotted as a function of monolayer composition in Fig. 1(b).

Fig. 1(a) shows a single sharp peak at a temperature of 183 K corresponding to melting of the adsorbed layer of pure nonane. This sharp peak moves to lower temperature (175 K) and broadens on addition of a small quantity of octane. Such a depression in melting point has been observed previously in adsorbed layers and in bulk alkane mixtures.[4,8] We attribute this broadening to the separation of the solidus and liquidus at this composition. The broadening in the peak remains on further addition of octane until a composition of $X_{\mathrm{oct}} = 0.6$–0.8 when the peaks narrow again, remaining narrow until the adsorbed layer is pure octane.

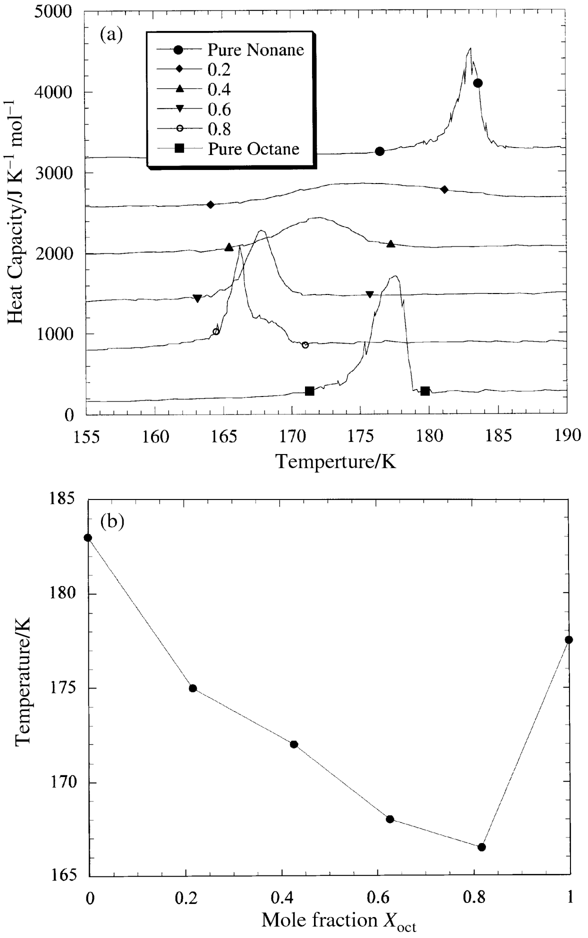

Fig. 1 (a) Adiabatic calorimetry from mixtures of octane and nonane adsorbed on graphite at a total coverage of 0.8 monolayers with octane mole fractions of 0, 0.217, 0.427, 0.626, 0.817 and 1.0. (b) Positions of the peaks in Fig. 1(a) as a function of monolayer composition.

The colorimetry data at $X_{\mathrm{oct}} = 0.8$ contains a sharp peak at 166 K but, significantly, also exhibits a shoulder at $T = 168$ K. We assign the lower temperature feature to a eutectic invariant.

It is interesting to determine the entropy increases through the melting transitions of the monolayers and to compare entropy changes with monolayer composition. These relative entropy changes can be calculated from C/T (C, heat capacity; T, absolute temperature) integrated with increasing temperature from some common reference temperature (125 K in this work) well below the transition. These entropy calculations are given in Fig. 2(a). By comparing the entropies at a temperature well above the monolayer transitions we can identify relative changes in entropy on monolayer melting with composition, given in Fig. 2(b).

Fig. 2(b) can be used to indicate the mixing behaviour of the monolayers if the liquid mixtures are assumed to be fully mixed. Melting of a mixed solid layer will have only an entropy of melting. This may vary slightly with composition but can be estimated as a simple linear sum of that of the two pure components (indicated by the diagonal dashed line in the figure). This trend does indeed appear to be followed for compositions $X_{\mathrm{oct}} = 0$–0.5 suggesting that over this composition

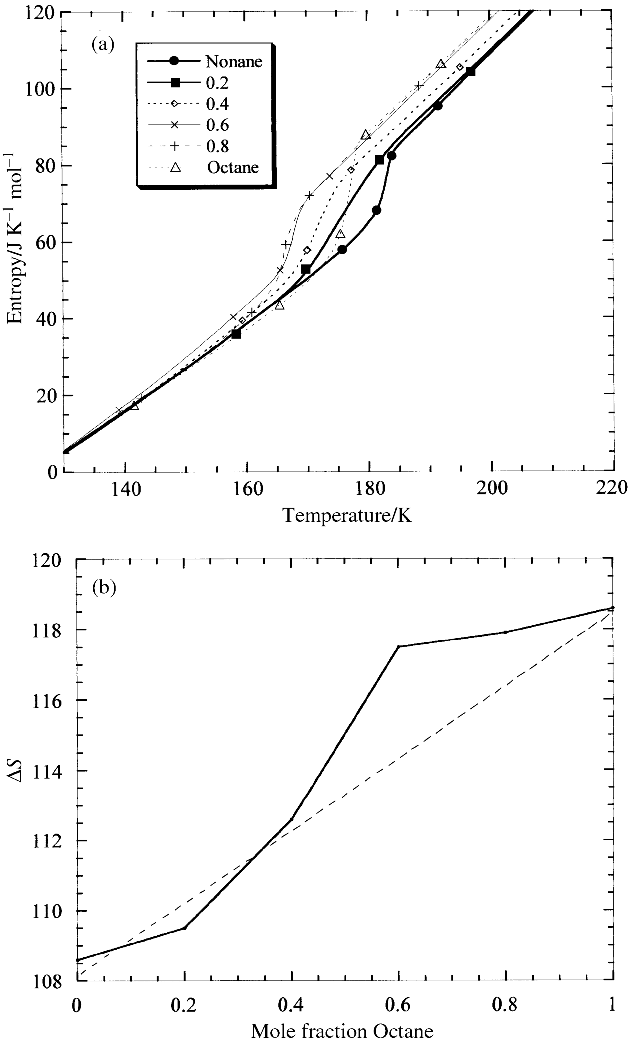

Fig. 2 (a) Relative entropy increment from 125 K (taken as zero) for the different monolayer compositions of Fig. 1(a). (b) The entropy increments at 200 K extracted from Fig. 2(a) for the different monolayer compositions. The diagonal dashed line indicates the entropy expected if mixtures are simple linear sums of the two pure components.

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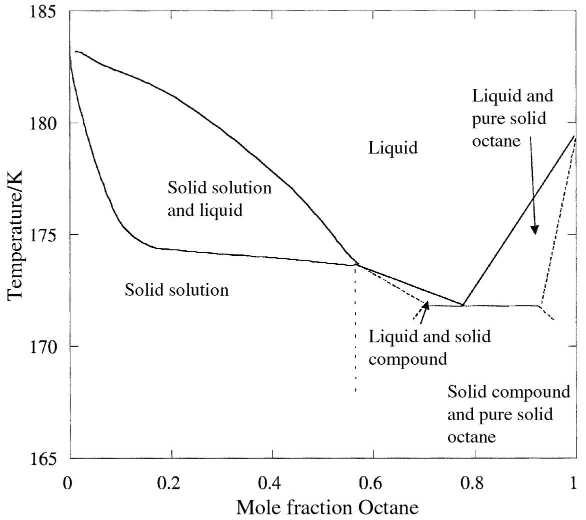

Fig. 3 Schematic phase diagram of submonolayer octane and nonane adsorbed on graphite. Composition of $X_{oct} = 0.55$ is a solid compound. Different regions of the phase diagram have been labelled with the appropriate phase(s).

range, on the nonane rich side of the phase diagram, there is a mixed solid monolayer.

However, if the solid state is not mixed then melting will have not only an entropy of melting but also an additional entropy of mixing. Therefore the entropy will exceed that of the simple linear sum, as illustrated on Fig. 2(b). This behaviour is observed for compositions $X_{oct} = 0.5$–1.0. This additional excess entropy can be estimated depending upon composition, X_{oct}:

$$\Delta S_{mis} = -R\{x_1 \ln x_1 + x_2 \ln x_2\}$$

Where $x_1 = X_{oct}$ and $x_2 = 1 - X_{oct}$. For a composition of $X_{oct} = 0.6$ the excess entropy would be 5.5 J K^{-1} mol^{-1}. The experimentally determined deviation from the fully mixed line is found to be 3.1 J K^{-1} mol^{-1}.

We now refine this estimate of the entropy to include the fact that the nonane rich side is in fact not pure nonane but a mixed crystal. The composition of this mixed crystal is estimated as follows: Many long alkanes form adsorbed layers with molecules that are parallel to each other[13] in lines. We assume a simple model for the mixed crystal containing lines of octane and lines of nonane molecules side by side. A line of nine octane molecules will have the same length as a line of eight nonane molecules; therefore the octane mole fraction in the mixed layer will be $X_{oct}^{mix} = 9/17 = 0.53$.

In a complete monolayer at a composition of $X_{oct} = 0.6$, 0.4 monolayers will be nonane. In a mixed crystal, this amount of nonane can include 0.45 monolayers of octane. 0.15 monolayers of pure octane cannot be included. The values of x_1 and x_2 to go into the calculation of the excess entropy are therefore $x_1 = 0.15$ and $x_2 = 0.85$ giving an excess entropy of 3.5 J K^{-1} mol^{-1}. This is in very good agreement with the experimental value of 3.1 J K^{-1} mol^{-1} given the simplicity of the model.

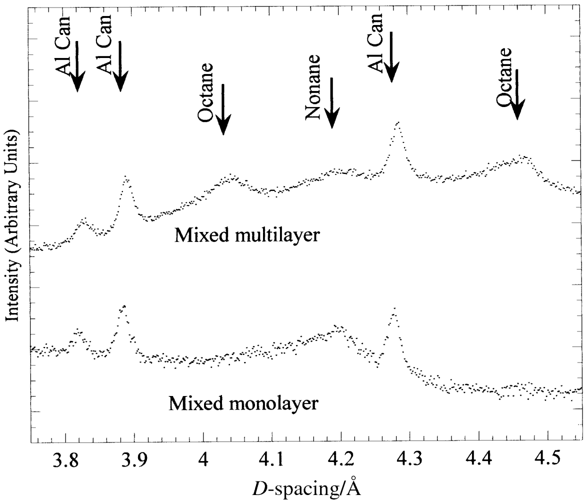

Fig. 4 OSIRIS neutron diffraction data from (top) a phase separated mixture of octane and nonane at multilayer coverages and (bottom) sub-monolayer coverage mixture of octane and nonane with mole fraction $X_{oct} = 0.5$. The arrows indicate the positions of peaks from the pure octane and pure nonane monolayers. The symmetrical peaks at *d*-spacings of 3.82, 3.88 and 4.28 Å in all patterns are from the aluminium sample can.

Thus we conclude, based on the calorimetry data, that octane and nonane will form a mixed solid monolayer over a wide range of composition, $X_{oct} = 0.0$–0.53, and form a solid molecular compound with a composition of approximately $X_{oct} = 0.53$. Above this composition there is phase separation of the material to essentially pure octane and the octane/nonane mixed crystal. This phase separation is evident from the excess entropy and the eutectic invariant evident in Fig. 1(a) at a temperature of 166.5 K. A schematic phase diagram representing these features is given in Fig. 3.

Neutron diffraction

Fig. 4 illustrates the scattering pattern from (top) a phase separated octane–nonane mixture at multilayer coverages, showing the peaks from pure octane and pure nonane monolayers and those from the aluminium sample can (labelled in the figure). Fig. 4 (bottom) shows the scattering pattern from an octane–nonane mixture at sub-monolayer coverage and a surface mole fraction of $X_{oct} = 0.5$. It is clear from the lower trace that there is no evidence of the pure octane peaks. This indicates that there is a mixed phase at this sub-monolayer coverage and mole fraction, in agreement with the adiabatic calorimetry results above. In the mixed phase there is only a single peak observed at approximately the position of the pure nonane monolayer peak. This again supports the conclusion that octane molecules are incorporated into the lattice of the longer nonane molecule as indicated by the adiabatic calorimetry data. The limited accessible range of *d*-spacing on OSIRIS means that a full structural characterisation of the mixed phase is not currently possible.

Discussion and conclusions

In this work we have provided a combination of calorimetry and diffraction data to demonstrate the mixing behaviour of solid monolayers of octane and nonane adsorbed on graphite at sub-monolayer coverage. Over a significant composition range it is found that the two components do mix on the surface, in marked contrast to the behaviour found at higher coverages.[8] There is a solid molecular compound formed with a composition of approximately $X_{oct} = 0.53$, with the shorter octane molecules incorporated into the lattice of the longer alkane nonane. We propose that at higher mole fractions than $X_{oct} = 0.53$ phase separation occurs because the nonane lattice is 'full'. This behaviour is identified by the calorimetry data and simple structural arguments.

The mixing behaviour in bulk alkanes has been investigated[14] and can be summarised in simple terms as follows: where the crystal symmetry of the pure components are different mixing is not preferred. For example, binary mixtures of the shorter alkanes C_{11}–C_{12}, C_{12}–C_{13}, C_{13}–C_{14}, C_{14}–C_{15} and C_{15}–C_{16} show a pronounced minimum in the phase diagrams indicating non-ideal behaviour[15] arising from the different space groups of the pure compounds (even members are usually triclinic and odd members orthorhombic). Even when the crystal symmetries of the two pure compounds are the same, mixing can still be prevented if the unit cells of the two lattices are significantly different in size. The bulk behaviour of octane and nonane reflects this behaviour as, although they are both triclinic, they still show a pronounced minimium in the melting curve. Previously we have demonstrated that, at higher, multilayer coverages, octane and nonane adsorbed layers follow these simple rules and phase separate because the symmetries of the unit cells are different.[8]

The phase behaviour of adsorbed alkanes at coverages around a monolayer is complex. In particular, many are found to be expanded at low, sub-monolayer coverages relative to the high coverage structures.[16] Such an expansion suggests that close packing criteria are relaxed in the structures and there may be additional space in the layer to accommodate molecules of a different kind.

The diffraction data presented here suggest that it is the shorter octane molecules that fit into the lattice of the longer nonane molecules, as might be expected. If there were a 'one-for-one' replacement of nonane molecules by octane this would create gaps in the lattice corresponding roughly to a CH_2 unit per octane molecule. However, in certain arrangements the octane can be incorporated without gaps—for example if there were 'lines' of octane molecules parallel to 'lines' of nonane molecules. In contrast, replacing octane molecules by nonane would require distortion of the whole lattice to accommodate them as the space available is too small.

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References

1 K. W. Herwig, B. Matthies and H. Taub, *Phys. Rev. Lett.*, 1995, **75**, 3154.
2 H. Kern and G. H. Findenegg, *J. Colloid Interface Sci.*, 1980, **75**, 346.
3 A. J. Groszek, *Proc. R. Soc. London Ser. A*, 1970, **314**, 473.
4 M. A. Castro, S. M. Clarke, A. Inaba, T. Arnold and R. K. Thomas, *J. Phys. Chem. B*, 1998, **102**, 10528.
5 E. P. Gilbert, P. A. Reynolds, P. Thiyagarajan, D. G. Wozniak and J. W. White, *Phys. Chem. Chem. Phys.*, 1999, **1**, 2715.
6 K. Morishige, Y. Takami and Y. Yokota, *Phys. Rev. B*, 1993, **48**, 8277.
7 P. Smith, R. M. Lynden-Bell and W. Smith, *Mol. Phys.*, 2000, **98**, 255.
8 M. Castro, S. M. Clarke, A. Inaba, T. Arnold and R. K. Thomas, *Phys. Chem. Chem. Phys.*, 1999, **1**, 5017.
9 M. A. Castro, S. M. Clarke, A. Inaba and R. K. Thomas, *J. Phys. Chem. B*, 1997, **101**, 8878.
10 S. M. Clarke, A. Inabak, T. Arnold and R. K. Thomas, *J. Therm. Anal. and Calorim.*, 1999, **57**, 641.
11 J. K. Kjems, L. Passell, H. Taub, J. G. Dash and A. D. Novaco, *Phys. Rev. B*, 1976, **13**, 1446.
12 M. A. Castro, S. M. Clarke, A. Inaba, C. C. Dong and R. K. Thomas, *J. Phys. Chem. B*, 1998, **102**, 777.
13 J. P. Rabe and S. Buchholz, *Science*, 1991, **253**, 424.
14 A. I. Kitaigorodskii, *Mixed Crystals*, Springer Verlag, Berlin, 1984.
15 P. Espeau, Y. Hagety, M. A. Cuevas-Diarte and H. A. J. Oonk, in *Proceedings of the XXI J.E.E.P.* (Rouen, 1995).
16 H. Taub, in *The Time Domain in Surface and Structural Dynamics*, ed. G. J. Long and F. Grandjean, Kluwer, Dordrecht, 1988, vol. 228.