

## Preferential Adsorption from Binary Mixtures on Graphite: The *n*-Decane–*n*-Heptan-1-ol System

María D. Alba,<sup>†</sup> Miguel A. Castro,<sup>\*,‡</sup> Stuart Clarke,<sup>‡</sup> Santiago Medina,<sup>†</sup> Loic Messe,<sup>‡</sup> Carmen Millán,<sup>†</sup> M. Mar Orta,<sup>†</sup> and Ana C. Perdigón<sup>§</sup>

*Instituto Ciencia Materiales de Sevilla, Departamento Química Inorgánica, CSIC-Universidad de Sevilla, Avenida Américo Vespucio s/n, 41092 Sevilla, Spain, Department of Chemistry and BP Institute, University of Cambridge, Cambridge, CB3 0HZ United Kingdom, and Departamento Ingeniería Química y Química Inorgánica, Universidad de Cantabria, Avenida de los Castros s/n, 39005 Santander, Spain*

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The competitive adsorption of *n*-decane and *n*-heptan-1-ol adsorbed from the binary liquid mixture onto graphite has been studied using differential scanning calorimetry, incoherent quasielastic neutron scattering, and <sup>1</sup>H and <sup>2</sup>H nuclear magnetic resonance. 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. Incoherent elastic neutron scattering, IQNS, and nuclear magnetic resonance, NMR, data indicate that decane is preferentially adsorbed onto the surface over most of the composition range, heptanol being the principal surface component only at very high heptanol concentrations. NMR is proved, for the first time, to be an efficient tool to provide independent information on each component of the system.

### Introduction

Adsorbed monolayers in contact with liquid are a fundamental physicochemical problem and play an important role in many interfacial phenomena, such as lubrication and detergency.<sup>1,2</sup> Although this phenomenon is of great importance, from both applied and basic points of views, its characterization is extremely difficult largely because of the presence of two macroscopic bulk phases. The presence of the bulk liquid creates a buried interface that makes it difficult to obtain structural or other information about the adsorbed layers.

A combination of several experimental techniques has been applied during the past decade to provide detailed structural and compositional information on multicomponent systems adsorbed on graphite, including alkanes, alcohols, carboxylic acids, and amines. Within this methodology differential scanning calorimetry, DSC, is used to map the phase behavior with bulk solution composition. This technique allows identification of the phase transitions occurring at the solid–liquid interface but is limited by the fact that it cannot determine the composition of the monolayer nor characterize their structures. Incoherent elastic neutron scattering, IQNS, is also employed for identifying and characterizing monolayers adsorbed from pure materials and solutions. This technique provides 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.<sup>3,4</sup> Finally, complementary use of neutron and X-ray diffraction measurements gives detailed structural information from the 2D layers with lattice parameters, symmetry 2D space group, and atomic positions being obtained for each adsorbed monolayer.<sup>3–6</sup>

Although this methodology can be used to explore these systems, neutron scattering techniques require centralized

international facilities to produce the neutrons and the measurements are time consuming, costly, and difficult to carry out. Hence, there is great interest in developing complementary techniques that can survey the temperature and composition behavior more readily. Nuclear magnetic resonance, NMR, has recently proved to be an efficient tool to determine the phase transitions of adsorbed species and satisfactorily applied to study the behavior of *n*-dodecane adsorbed on graphite.<sup>7</sup> In summary, the technique exploits the ‘dynamic contrast’ between the ‘immobile’ adsorbed species and the mobile species in the bulk liquid. Significantly, the complementary information obtained from combining <sup>1</sup>H and <sup>2</sup>H NMR signals from both deuterated and protonated samples has indicated that this exciting methodology can be extended to the study of multicomponent systems and obtaining independent information on each component.

In this paper, we present data from a combination of techniques, including NMR measurements from multicomponent systems, for the first time on the binary mixture of decane and heptanol. Recent works have indicated that longer homologues of alkanes and alcohols are found to adsorb preferentially over their shorter homologues.<sup>8,9</sup> It has also been reported that the hydrogen bonding of alcohols leads to preferential adsorption over alkanes with the same alkyl chain length.<sup>9</sup> Hence, we explore the preferential adsorption behavior on the graphite surface of these two molecules, where there is expected to be a delicate balance of these forces. We also compare the NMR and IQNS results for these materials and include a discussion of the application of NMR to these adsorbed systems.

### Experimental Section

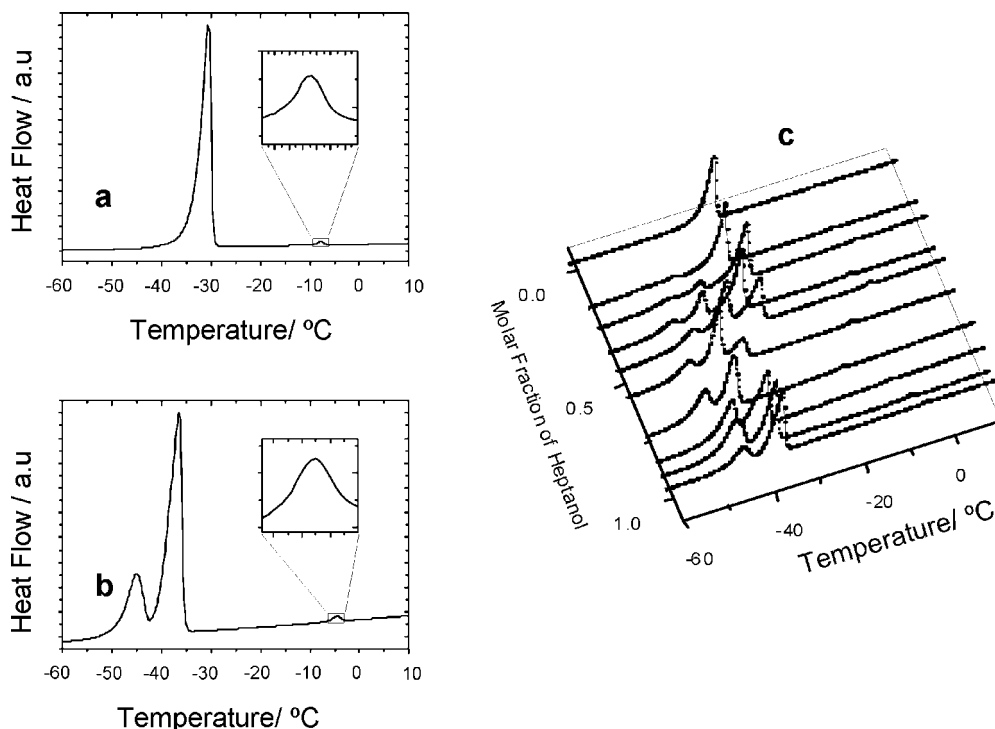
**Materials.** Two adsorbents were used in these experiments. Recompressed exfoliated graphite Papyex (Le Carbone Lorraine)<sup>10</sup> was employed for the calorimetry and incoherent neutron scattering measurements. A powdered and graphitized carbon black Carbopack B (Supelco Inc., Bellefonte)<sup>11</sup> was employed for the solid nuclear magnetic resonance experiments.

\* To whom correspondence should be addressed. Phone: +34 954559732. Fax: +34 954 559753. E-mail: macastro@us.es.

<sup>†</sup> CSIC-Universidad de Sevilla.

<sup>‡</sup> University of Cambridge.

<sup>§</sup> Universidad de Cantabria.



**Figure 1.** (a) DSC thermogram for 40 monolayers of decane adsorbed on graphite, (b) DSC thermogram for 40 monolayers of heptanol adsorbed on graphite, and (c) DSC thermograms for a mixture of decane and heptanol at different compositions.

The specific surface area of both specimens was determined by adsorption isotherm measurements using nitrogen, 31.6 and 98.1  $\text{m}^2 \cdot \text{g}^{-1}$ , respectively. Carbopack B adsorbent has been included in the present study along with the usual Papyex adsorbent, employed in previous studies, to provide a random distribution of particles required for NMR measurements, relative to the partially oriented Papyex samples ideal for diffraction studies.

Protonated and deuterated *n*-decane and protonated *n*-heptan-1-ol were obtained from Aldrich and used without further purification. The deuterated heptanol was prepared using isotope exchange of the corresponding carboxylic acid and reduction to the alcohol. The deuteration levels are estimated to be >98%.

Graphite substrates were outgassed under vacuum in an oven at 350 °C before known quantities of alcohol/alkane mixtures were added as liquid by microsyringe. The system was annealed onto the surface at a temperature of approximately 40 °C below the bulk boiling point. We express the amount of each adsorbed component in terms of the number of equivalent monolayers adsorbed. This is estimated from the areas per molecule, taken from Groszek<sup>12</sup> and Morishige,<sup>13</sup> and the specific surface area of the graphite. For the calorimetry measurements presented here the total coverage was approximately 40 monolayers. For IQNS and NMR measurements 8 monolayers of heptanol were used and successive amounts of decane added to achieve the different required compositions.

**Calorimetry.** Application of differential scanning calorimetry (DSC) for study of the phase behavior in adsorbed layers has been given elsewhere<sup>14</sup> and can be used to identify the temperatures for both bulk and monolayers transition adsorbed onto graphite. The DSC measurements were made on a Perkin-Elmer Pyris 1 series power compensation method calorimeter at the BP Institute, University of Cambridge. In all experiments the scan rate was typically 10°/min,<sup>15</sup> representing a compromise between sensitivity and temperature resolution.

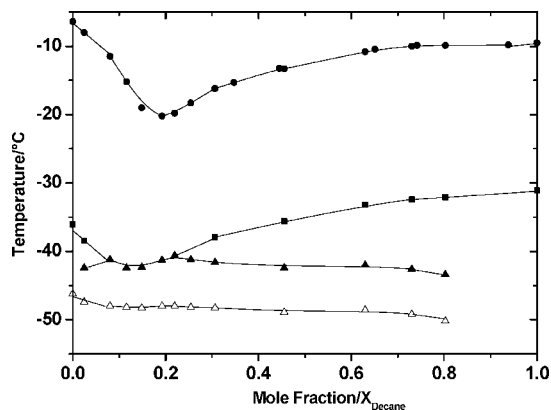
**Incoherent Neutron Scattering.** The high-resolution back-scattering spectrometer, IN10,<sup>16</sup> at the ILL, Grenoble, France,

with an energy resolution of approximately  $\pm 1.5 \mu\text{eV}$  was used for these experiments as described elsewhere<sup>17</sup> to provide direct evidence on the absolute composition of the monolayers in the binary mixtures. The incident wavelength was 0.6275 nm with both a monochromator and analyzer crystals of Si(111). The Doppler drive was turned off such that only elastically scattered neutrons reached the detectors. To avoid coherent scattering features, small-angle scattering, and diffraction peaks from the samples the detectors were placed at momentum transfer values of 5.97, 8.62, 14.16, and 16.40  $\text{nm}^{-1}$ , and cadmium masks were used to prevent diffracted neutrons from reaching the detectors. The momentum transfer is defined as  $(4\pi \sin \theta)/\lambda$ , with  $\lambda$  being the wavelength of the neutrons and  $\theta$  one-half the scattering angle. In the results that follow only data from one of the detectors are presented, the data from all detectors being similar.

**Solid Nuclear Magnetic Resonance.** Static  $^1\text{H}$  and  $^2\text{H}$  NMR measurements at 9.39 T were recorded on a Bruker DRX400 spectrometer at the NMR Research Service, Spectroscopics Service at ICMS (CSIC-University of Sevilla), equipped with a multinuclear probe and an analogical/digital ADC 2 MHz converter. The spectra were recorded at different temperatures after an equilibration time of 5 min. Longer equilibration times were tested during acquisition in order to ensure that the selected time was long enough.  $^1\text{H}$  and  $^2\text{H}$  NMR spectra were obtained using a single pulse sequence and typical  $\pi/2$  pulse widths of 4.1  $\mu\text{s}$  and a pulse space of 5 s for  $^1\text{H}$  and typical  $\pi/2$  pulse widths of 4.9  $\mu\text{s}$  and a pulse space of 4 s for  $^2\text{H}$ .

## Results and Discussion

**Calorimetry.** Figure 1 includes the DSC thermograms for the pure decane (Figure 1a) and heptanol (Figure 1b) adsorbed on graphite and a 3D projection (Figure 1c) illustrating thermograms at a number of compositions across the phase diagram. All DSC thermograms are plotted such that an upward peak corresponds to an endothermic transition and, for the temperature range investigated, there are no features from



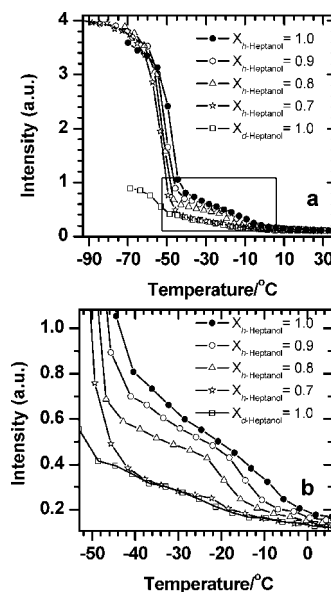
**Figure 2.** Phase diagram for the heptanol/decane system in the presence of graphite as a function of solution composition determined from the DSC measurements: (●) monolayer transition, (Δ) solid–solid transition of heptanol, (▲) eutectic bulk transition, and (■) bulk liquidus transition.

graphite alone, the observed signals arising from the adsorbed materials alone.

The large endothermic transitions from the bulk adsorbates are readily distinguished from the much smaller, high-temperature melting points of the solid adsorbed monolayers,<sup>18</sup> the latter appearing approximately 10% higher in absolute temperature than the bulk.<sup>19</sup> Thus, for decane, Figure 1a, the graph has two peaks. The high-intensity peak shown at lower temperature, close to the bulk melting point of pure decane in the absence of graphite, is assigned to the bulk adsorbate. The low-intensity second peak, also expanded in Figure 1a, appears at temperatures above the bulk melting point and is not present in the DSC trace of either pure decane in the absence of graphite or graphite alone, and it is assigned to melting of the adsorbed monolayer on graphite. This feature has been reported previously, and its assignment to a solid monolayer melting transition has been confirmed by diffraction and IQNS. A similar interpretation can be made from the heptanol data, Figure 1b. In this case, however, two high-intensity peaks can be observed at low temperatures. While the second one, centered at around  $-37^{\circ}\text{C}$ , is close to the bulk melting point for heptanol, the first one, ca.  $-46^{\circ}\text{C}$ , is interpreted as a solid–solid transition.<sup>18</sup>

Figure 1c shows the changes produced in the DSC thermograms as a function of the absolute composition of the heptanol–decane mixtures. In order to clarify these variations, Figure 2 illustrates the transition temperatures observed for each composition. Three signals can be observed for the low-temperature region (below  $-30^{\circ}\text{C}$ ) and discussed in terms of bulk transitions for a eutectic system. A first signal, occurring between  $-46$  and  $-48^{\circ}\text{C}$  and marked with open triangles, corresponds to the solid–solid transition of heptanol and only is reduced in intensity as heptanol concentration diminishes. At around  $-43^{\circ}\text{C}$  a second signal marked as solid triangles is identified in many of the samples and interpreted as the eutectic invariant of the bulk melting transition. Finally, the bulk liquidus transition is marked with solid squares. The eutectic composition is determined to be at a mole fraction of decane of approximately 0.15.

The monolayer melting transition, responsible for the low-intensity feature at high temperatures, also shows distinctive composition dependence similar to the bulk behavior, although the minimum is more pronounced and occurs at a slightly different composition (mole fraction of decane = 0.20). It is important to note that DSC is unable to distinguish which component or mixture of components is adsorbed at any

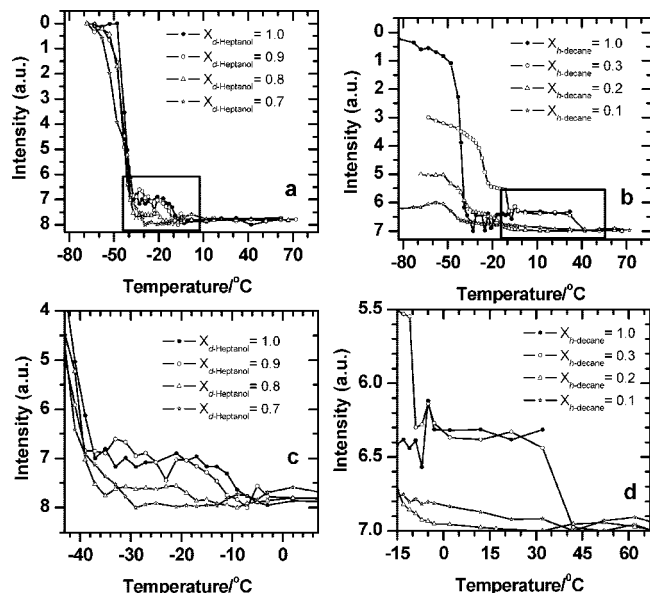


**Figure 3.** (a) IQNS data from heptanol/decane mixtures adsorbed on graphite as a function of temperature for a range of solution compositions. (b) Expanded plot for the monolayer area.

composition, except at the limits of the pure single components. The effect of preferential adsorption is to shift the data horizontally across the phase diagram. Hence, the eutectic temperature would be unchanged, but the eutectic composition in the monolayer cannot be determined from this figure.

**Incoherent Elastic Neutron Scattering.** Figure 3a shows the intensity of the elastic peak as a function of temperature for 8 monolayers of *h*-heptanol adsorbed on graphite and after successive addition of *d*-decane to the *h*-heptanol sample to achieve the required composition. Since the contribution from protonated components dominates the incoherent scattering and the contribution from the deuterated components will always be relatively small,<sup>20</sup> the IQNS data obtained here are essentially determined by the *h*-heptanol component. At the lowest temperatures in the figure all the heptanol, bulk, and monolayer phases is solid and gives a strong signal. As the bulk melting point (ca.  $-63^{\circ}\text{C}$ , 210 K) is approached, the intensity of the elastic peak begins to fall, falling particularly rapidly over the range 200–220 K ( $-73$  to  $-53^{\circ}\text{C}$ ). However, just above the bulk melting point not all the elastic intensity has disappeared, the remaining intensity corresponding to the solid monolayer. The signal reaches the background at about 280 K ( $7^{\circ}\text{C}$ ). The temperatures of the transitions are in reasonable agreement with those observed by DSC.

An estimate of the amount of solid at just above the bulk melting point can be made from the ratios of intensities of the elastic scattering at this temperature and at the lowest temperature where all heptanol is solid.<sup>8</sup> In Figure 3b an expansion of the monolayer transition region is shown, and it illustrates that there is a significant decrease in the level of the residual intensity corresponding to the solid monolayer, clearly indicating that the amount of solid *h*-heptanol in the monolayer is falling as decane is added. This result indicates that there is a preferential adsorption of decane over the heptanol and provides a quantitative measure of the variation in surface composition with variation in bulk solution composition. Complete displacement of heptanol requires only small quantities of decane such that by a composition of  $X_{\text{heptanol}} = 0.70$  ( $X_{\text{decane}} = 0.30$ ) there is almost no *h*-heptanol on the surface. The additional stability provided by the hydroxyl group in the heptanol molecule is



**Figure 4.** (a)  $^2\text{H}$  MAS NMR data from *d*-heptanol/*h*-decane mixtures adsorbed on graphite as a function of temperature for a range of solution compositions. (b)  $^1\text{H}$  MAS NMR data from *d*-heptanol/*h*-decane mixtures adsorbed on graphite as a function of temperature for a range of solution compositions. (c) Expanded plot of a for the monolayer area. (d) Expanded plot of b for the monolayer area.

neutralized by the higher alkyl chain length in the decane molecule. 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 alcohol.

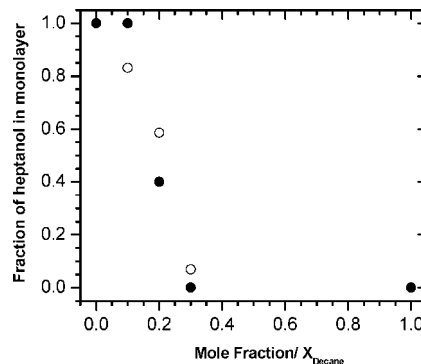
**Solid-State Nuclear Magnetic Resonance.** Solid-state multi-nuclear magnetic resonance gives direct information on the presence of adsorbed solid monolayer because of the drastically different NMR response of a compound depending on its mobility and composition.<sup>21,22</sup> NMR of a liquid sample results in narrow-line spectra since the effects of certain nuclear magnetic interactions are averaged to zero owing to the rapid and random motion of molecules in liquids. For solids or other immobile systems like tightly bound adsorbed species the above-mentioned nuclear spin interactions are not averaged, leading to large line broadening in the experimental data.

Figure 4 displays the maximum intensity values for the  $^2\text{H}$  and  $^1\text{H}$  NMR signals, corresponding to a *d*-heptanol/*h*-decane binary mixture adsorbed on graphite. The intensities were determined by numerical integration of the  $^2\text{H}$  and  $^1\text{H}$  peaks. The total amplitude loss observed during the temperature increase due to Curie's law and  $Q$  factor effects on excitation and detection<sup>23,24</sup> have been corrected.

In order to interpret the data from a more quantitative point of view two considerations can be made: (a) the areas under the NMR signals from all spectra obtained from a given system should be constant and proportional to the number of NMR-active species<sup>25</sup> and (b) the strong enhancement of the line widths at the lower temperatures is caused by the reduction in the mobility of the NMR-active species and should be assumed to indicate the onset of the 2D solid–liquid phase transition.<sup>26</sup> In that case, the NMR resonance line width is expected to be given approximately by

$$\delta\nu = \alpha_s(\delta\nu)_s + (1 - \alpha_s)(\delta\nu)_l$$

where  $(\delta\nu)_s$  and  $(\delta\nu)_l$  are the line widths in the 2D solid monocrystallites and in the liquid, respectively, and where  $\alpha_s$  and  $(1 - \alpha_s)$  are the corresponding fractional lifetimes or,



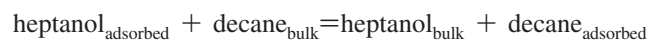
**Figure 5.** Surface composition of the heptanol/decane mixture adsorbed on graphite as a function of bulk composition deduced from IQNS data (○) and NMR data (●).

equivalently, the fractions of molecules in the solid and liquid phases.

The plots corresponding to Figure 4a and 4b show, from both  $^2\text{H}$  and  $^1\text{H}$  signals, the existence of a two-step process. In the first part, at temperatures above 240 K,  $-33\text{ }^\circ\text{C}$ , for *d*-heptanol (Figure 4a) and above 260 K,  $-13\text{ }^\circ\text{C}$ , for *h*-decane (Figure 4b) an increase in the intensity with a coincident drastic reduction in the line width of the signal (available as Supporting Information) are observed. It indicates a major mobility of the *d*-heptanol and *h*-decane bulk phases. This first step is associated with the bulk melting of both components of the binary mixture. From these temperatures a set of almost constant values is observed in both graphs and should be attributed to the existence of a remaining 2D solid phase. Finally, at temperatures above 280 K,  $7\text{ }^\circ\text{C}$ , for *d*-heptanol (Figure 4a) and above 310 K,  $37\text{ }^\circ\text{C}$ , for *h*-decane (Figure 4b) a further increase of the intensity values is caused by the melting of the 2D solid phase.

An estimate of the amount of solid which remains just above the bulk melting point can be made as reported elsewhere.<sup>7</sup> In Figure 4c and 4d an expansion of the second transition region is shown, and the results again indicate that only a single solid monolayer survives on the graphite surface in good agreement with previous incoherent elastic neutron scattering measurements. In this region the intensity of the  $^2\text{H}$  and  $^1\text{H}$  signals decrease as the amount of *h*-decane or *d*-heptanol increases in the mixture. The decrease is more evident in the  $^2\text{H}$  signal, which indicates that there is preferential adsorption of decane and a quantitative measure of the variation in surface composition with variation in bulk solution composition is possible.

As stated above, it is possible to analyze the surface composition of the heptanol/decane mixture adsorbed on graphite from the IQNS and NMR results. A comparison of the fraction of solid heptanol in the monolayer from both IQNS data (open circle) and NMR data (solid circle) as a function of bulk composition has been plotted in Figure 5. We note that here is very good agreement between the results of both techniques. It is also evident that by a composition of  $X_{\text{decane}} = 0.30$ , the *h*-heptanol is essentially completely displaced by decane on the graphite surface. Additionally, we also used NMR data to calculate the equilibrium constant value,  $K$ , for the preferential adsorption of decane over heptanol as defined by the following equilibrium<sup>27</sup>



and we find a value of 7.88, again in reasonable agreement with that determined by IQNS (3.22) and DSC<sup>9</sup> (7.5).



## Conclusions

This paper clearly demonstrates that NMR techniques can provide an efficient tool to determine the phase transitions of adsorbed multicomponent systems and provide independent information on each component of the system even where the components are very similar. It is possible by the combined use of protonated and deuterated materials, which allows us to analyze the different behavior of mixed components with similar  $^1\text{H}$  chemical shift values.

Combination of results from calorimetry, incoherent neutron scattering, and solid-state nuclear magnetic resonance data shows that heptanol and decane do not mix on the surface of graphite. The behavior of the melting point suggests a two-dimensional eutectic. The incoherent scattering data and solid-state NMR data show that decane is preferentially adsorbed and that over most of the composition range there is essentially very little heptanol present.

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**Supporting Information Available:** This material is available free of charge via the Internet at <http://pubs.acs.org>.

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