



The structure of *n*-alkane binary mixtures adsorbed on graphite

Philippe Espeau^{a,*}, John W. White^b, Robert J. Papoular^c

^a *Laboratoire de Chimie Physique et Minérale, Faculté de Pharmacie, Université René Descartes-Paris V, F-75006 Paris, France*

^b *Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia*

^c *Laboratoire Léon Brillouin, CEA-CEN Saclay, F-91191 Gif-sur-Yvette Cedex, France*

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Abstract

The thermodynamics and structure of the surface adsorbed phase in binary C15–C16 and C15–C17 *n*-alkane mixtures confined in graphite pores have been studied by differential scanning calorimetry and small-angle X-ray scattering. The previously observed selective adsorption of the longer alkane for chain length differences greater than five carbon atoms is verified but reduced for chain length differences less than or equal to two. With a difference in chain length of one carbon atom, Vegard's law is followed for the melting points of the adsorbed mixture and the (0 2) *d*-spacing is a continuous function of the mole fraction *x*. With a two-carbon atom difference, samples aged for 1 week have a lamellar structure for which the entities A_{1–x}B_x try to be commensurate with the substrate. The same samples aged for 1 month show a continuous parabolic *x*-dependence for both the melting points and the *d*-spacings. An explanation in terms of selective probability of adsorption is proposed based on crystallographic considerations.

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1. Introduction

In binary mixtures of alkanes differing by more than a few carbon atoms in length, preferential adsorption of the longer alkane is observed at a graphite surface [1,2]. Such preferential adsorption has also been detected for short chain hydrocarbons by

neutron diffraction [3]. This is due to the increase of the enthalpy of adsorption, ΔH_a , with the chain length [4] and possibly to an increasing incompatibility of the alkanes, which has been shown to cause microphase separation in the bulk solids [5,6]. ΔH_a for a given alkane also increases as the adsorption temperature approaches the freezing point of the bulk alkane. The strong lateral interactions of the adsorbed long-chain molecules, caused by alignment and close packing of the chains parallel to the graphite basal plane, contribute to this effect. Mixtures of alkanes featuring

* Corresponding author. Tel.: +33 1 53 73 96 76;

fax: +33 1 53 73 96 76.

E-mail address: philippe.espeau@univ-paris5.fr (P. Espeau).

a chain length difference between the two *n*-alkanes in solution longer than five carbon atoms [3,7–10] have already been extensively studied. Here, we look at the fractionation behaviour of alkanes differing by only one- or two-carbon atoms.

In most of the previous work, the alkane was dissolved in a solvent (short chain alkane or other) and allowed to come to equilibrium with the graphite surface. Aveyard [7] measured the coverage of the graphite surface by octane (C₈H₁₈) + hexadecane (C₁₆H₃₄) at different mole fractions of hexadecane (the chain length difference Δn between both alkanes is equal to 8). A coverage of approximately 1 is reached at a mole fraction of C₁₆H₃₄ of about 0.3. Below $x = 0.3$, the longer alkane is still preferentially adsorbed and the coverage increases rapidly when the concentration of hexadecane in solution increases.

The systems investigated here are C₁₅H₃₂–C₁₆H₃₄ and C₁₅H₃₂–C₁₇H₃₆ (i.e. $\Delta n = 1$ and 2, respectively). In the following, we label the alkane as C_{*n*} instead of C_{*n*}H_{2*n*+2}. Our primary objective is to determine if the graphite substrate preferentially adsorbs the longer alkane or if, on the other hand, both components are adsorbed in the same proportion as their concentrations in the mixture.

2. Experimental

n-Alkanes from Aldrich, of nominal purity 99%, were used without any further purification. Low density graphite, papyex, (3.5 mm and 12.7 mm diameter disks) was used for both the DSC and X-ray experi-

ments, prepared as in previous experiments [11,12]. These graphite disks were outgassed at 10^{−4} mbar for 24 h at 250 °C [11,12] and thoroughly degassed mixtures of *n*-alkanes introduced into the graphite pores from the melt. The samples were then equilibrated at a temperature 30 °C above the melting point of the binary mixtures. Both the thermodynamic and crystallographic behaviours of the adsorbed phase have been studied. Differential scanning calorimetry (TA Instruments DSC 2920 Modulated) was used for the former and small-angle X-ray scattering [SAXS] (ELLIOT GX13 rotating anode X-ray generator with Huxley–Holmes monochromator, wavelength $\lambda = 1.54 \text{ \AA}$ [13,14]) for the latter. A scanning rate of 5 K min^{−1} was used for the DSC experiments. Indium, naphthalene and water were used for calibration of the DSC in the same experimental conditions as for this study.

Up to 15 different mole fractions were analysed for each system. For each case, three samples of the same mole fraction were prepared. The graphite pores were fully filled by the molten mixtures. The structure of the adsorbed phase was measured about 5 °C above the liquidus temperature of the bulk solid alkane mixture. With DSC, the samples were measured from the melting point of the “included” phase (also called “bulk” phase in ref. [11]) to the melting of the last adsorbed phase.

3. Pure components

In all cases the melting behaviour of the bulk solids was studied and Table 1 displays the observed bulk

Table 1

Bulk transition temperatures (the solid–solid transitions are orthorhombic → RI and the solid–liquid transitions are RI → liquid for the odd alkanes and triclinic → liquid for the even ones) and melting temperatures of the adsorbed layer in contact with the graphite surface T_{fusion} for the three studied *n*-alkanes

	Reference	C15	C16	C17
$T_{\text{solid–solid}}$ (°C)	This work	−2.8 ± 0.4		+11.1 ± 0.4
	[15]	−2.3		
	[16]	−2.8		+11.1
	[17]			+10.5
$T_{\text{solid–liquid}}$ (°C)	This work	+9.4 ± 0.5	+17.4 ± 0.3	+20.9 ± 0.7
	[15]	+9.9	+18.2	
	[16]	+9.6	+17.6	+21.6
	[17]			+21.7
T_{fusion} (°C)	This work	+46.4 ± 0.5	+54.4 ± 0.5	+61.8 ± 0.5

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