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Regular Article

Phase separation of carboxylic acids on graphite surface at submonolayer regime

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Abstract. Mixing behaviour of solid crystalline monolayers adsorbed onto graphite from different mixtures of undecanoic and dodecanoic acids at submonolayer coverage has been investigated. X-ray diffraction measurements have been collected from a variety of compositions as a function of temperature. An extensive phase separation is found for all the compositions – the scattering patterns characteristic of the pure material crystalline structures being preserved across the entire composition range. The temperature dependence of the monolayer melting points and their depression is also clearly indicative of separation of the two surface components, in clear contrast to that expected if the two carboxylic acids mixed ideally in the monolayer.

1 Introduction

The physisorption of simple molecules, such as alkanes, alcohols or carboxylic acids, to solid surfaces is of great importance for both academic and industrial purposes [1]. The structural and compositional behaviour of these layers is often very different to their bulk behaviour as consequence of a delicate balance of adsorbate and surface interactions. In particular, many systems are found to adsorb solid, crystalline monolayers at temperatures where the bulk phases are liquids or solutions [2].

Carboxylic acids are an industrially important class of adsorbates as a major component of greases and lubricants [3]. In these cases, it is important to identify which species are adsorbed from mixtures and, if co-adsorption occurs, whether different acids mix or phase separate in the solid layer. Here we consider the behaviour of two carboxylic acids adsorbed onto graphite. Initial structural investigations have demonstrated carboxylic acids do indeed adsorb from their liquids to form crystalline close-packed monolayers on graphite at temperatures above the bulk melting point. Interestingly the linear alkyl carboxylic acids are found to exhibit a pronounced odd-even effect in their solid monolayer crystal structures and the monolayer melting points [4].

The mixing behaviour of simple linear alkyl carboxylic acids has also been investigated at high coverages. In outline, it is found that binary acid mixtures with components that have alkyl chains that differ by two or three methylene groups exhibit a significant degree of phase separation in the monolayer [5]. A regular solution model has been proposed to interpret this mixing/phase separation behaviour with one parameter that is related to the interadsorbate interaction energies and another parameter to include the extent of preferential adsorption [6].

In this work, we report X-ray results from the undecanoic – dodecanoic system at submonolayer regime as a function of the temperature. This clearly contrasts with previous work at

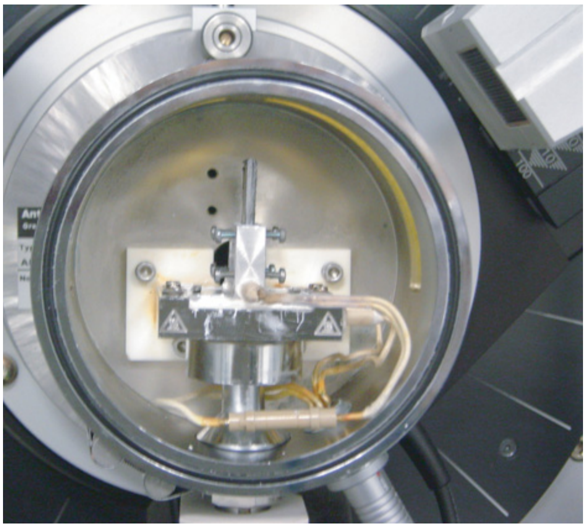

Fig. 1. Instrumental modification of the Anton Paar TTK450 low-temperature camera for transmission geometry. A graphite sample is located in the sample holder.

higher coverages, but also enables us to probe the surface behaviour in more details as the scattering patterns are not compounded by the presence of 'bulk' adsorbate. Here we include a comparison of the scattering patterns of the binary mixtures with the crystalline structures adopted by the pure components. This enables us to identify the monolayer mixing behaviour. In addition, by extracting the temperature dependence of the diffraction patterns we can obtain the monolayer melting point as a function of composition which also provides an independent indicator of the monolayer mixing behaviour.

2 Experimental

The adsorbent used in these experiments was recompressed exfoliated graphite Papyex (Le Carbone Lorraine) [7] with a specific surface area of $31.6\,\mathrm{m}^2\cdot\mathrm{g}^{-1}$ determined by adsorption of nitrogen. Undecanoic ($C_{11}H_{22}O_2$, CAS: 112-37-8) and dodecanoic ($C_{12}H_{24}O_2$, CAS: 143-07-7) carboxylic acids were obtained from Sigma Aldrich at 99% purity and they have been used without further purification. The graphite substrates were outgassed under vacuum in an oven at 350 °C before known quantities of the adsorbates were added and annealed at a temperature just below the dodecanoic acid bulk boiling point (225 °C). Total coverages were maintained at 0.9 of a monolayer in all the experiments. The amount required to achieve the required coverage for each component was estimated from the area per molecule (using the Groszek model [8,9]), values of $79.25\,\mathrm{Å}^2$/molecule for undecanoic and $86\,\mathrm{Å}^2$/molecule for dodecanoic, and the specific surface area of the graphite.

X-ray experiments were recorded with an Anton Paar TTK 450 low-temperature camera (Anton Paar, Austria) attached to a Bruker D8 Advance diffractometer (Bruker, Germany), modified for symmetrical transmission geometry at CITIUS, University of Sevilla, Spain as shown in Figure 1. Single rectangular sheets of graphite, of approximately $15\,\mathrm{mm}\times 30\,\mathrm{mm}\times 2\,\mathrm{mm}$ dimensions and 1 g weight, were irradiated by copper Kα radiation. The device uses θ/θ X-ray tube and detector movement to maintain the momentum transfer in the plane of the graphite sample.

3 Results and discussion

Figure 2 presents the XRD patterns measured between 17 and 22 ° 2θ as a function of temperature for 0.9 monolayers of undecanoic acid, dodecanoic acid and some binary mixtures on

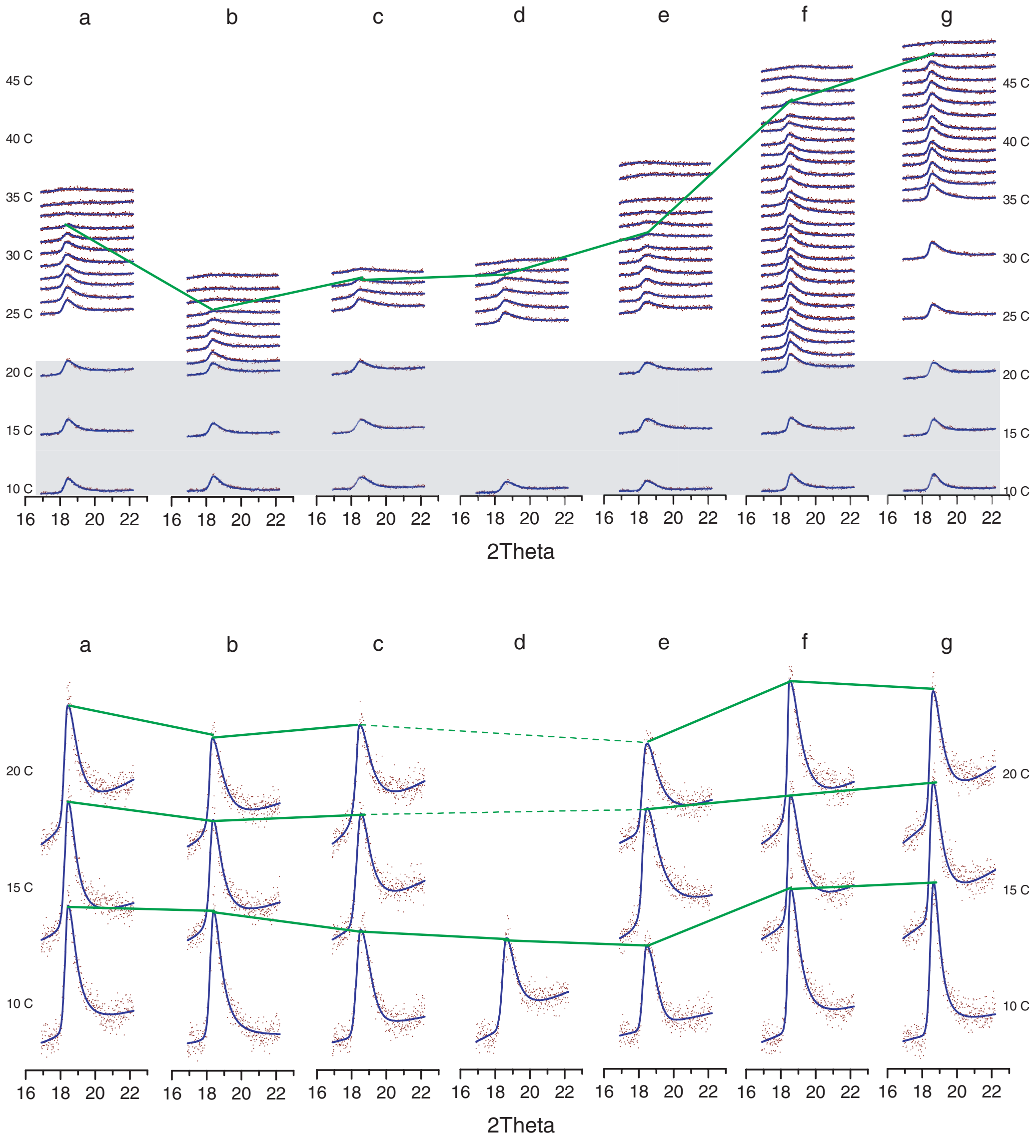

Fig. 2. Top: experimental X-ray diffraction patterns (points) and best fitting functions (lines) for undecanoic acid, C11 (left hand side), dodecanoic acid, C12 (right hand side) and their binary mixtures adsorbed onto graphite at a total coverage of 0.9 monolayers and the following mole fractions: (a) C11 1.0, C12 0.0; (b) C11 0.8, C12 0.2; (c) C11 0.6, C12 0.4; (d) C11 0.5, C12 0.5; (e) C11 0.4, C12 0.6; (f) C11 0.2, C12 0.8; (g) C11 0.0, C12 1.0. Temperatures are indicated at right and lefts margins. An eye-guided line indicates the 2D melting for each composition. Bottom: zoomed area from the grey-shadowed box from top graph including the X-ray diffraction patterns for 10°–20 °C temperatures. Eye-guided lines indicate the evolution of the peak intensity with composition for each temperature.

graphite. Experimental data are represented with red points and fitted functions are continuous blue lines. This 2θ range includes the highest 2D peak for the two pure phases analysed as previously described [4]: undecanoic structure has a rectangular cell of 32.7 Å × 9.7 Å dimensions, 2D space group of symmetry *pgg* and four molecules per unit cell. The structure corresponding to dodecanoic acid has an oblique cell with values of 17.9 Å × 9.6 Å and β 100°, 2D symmetry *p2* and two molecules per unit cell. Both structures have a zig-zag configuration with their carbon skeleton parallel to the graphite surface.

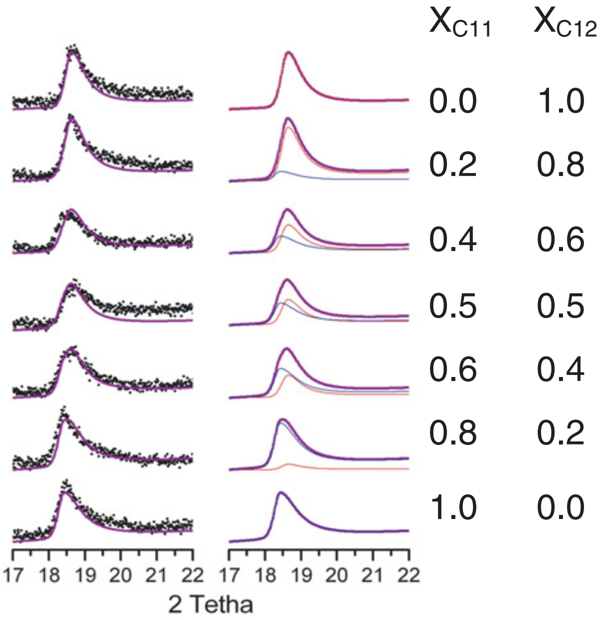

Fig. 3. Left: experimental XRD patterns (black circles) and fitted functions (purple lines) obtained from linear combinations of those employed for the pure components for different compositions of the undecanoic – dodecanoic system adsorbed onto graphite at a total coverage of 0.9 monolayers (bottom: pure undecanoic). Right column: fitted functions (purple lines) showing the contribution of each component (blue lines for undecanoic acid and red lines for dodecanoic acid).

The extreme hand left set of data is for undecanoic acid on its own. The characteristic 2D peak, centred at 18.3° 2θ in the 10 °C pattern is assigned to the $(-1, 2)$ reflection, in agreement with previously reported data. As the temperature increases, two observations can be made: at the lowest temperature range (10–25 °C), the 2D peak is shifted to slightly lower 2θ values due to the thermal lattice expansion; at the highest temperature range (26–32 °C), as the 2D melting point is approached, the 2D peak is broadened indicating either a smaller domain size or a higher degree of disorder. Finally, at 33 °C, the disappearance of the 2D peak indicates the complete melting of the monolayer. A similar behaviour can be observed for dodecanoic acid at the right end of Figure 2. The $(-1, 2)$ 2D peak for this phase, centred at 18.7° 2θ in the 10 °C pattern, has disappeared at 47 °C, in agreement with the higher 2D melting transition described previously for dodecanoic acid adsorbed onto graphite.

Columns b–f in Figure 2 show the XRD patterns obtained for the mixtures of C11 and C12 acids. Close inspection of the data in Figure 2 indicates that the 2D peak observed for all the compositions is modified in both its profile parameters (intensity, position and width) and the temperature at which disappears (i.e. the 2D melting point) with changes in composition. In order to show more clearly the shape and intensity variation of the 2D peak, Figure 3 includes the XRD patterns for the whole set of compositions at the lowest temperature examined. The experimental data, represented by black points in the left column, shows a reduction of the peak intensity and an increase of the peak width for mixed compositions (X_{C11} 0.6, X_{C12} 0.4; X_{C11} 0.5, X_{C12} 0.5; and X_{C11} 0.4, X_{C12} 0.6) with similar concentrations of each component. Compositions with a high concentration of one component, 0.8 : 0.2 and 0.2 : 0.8, resembles much more the 2D peak obtained for the pure components.

If the system is phase separating then we simply expect the diffraction patterns of mixtures to be the linear sum of the contribution sum of the pure component scattering patterns. Hence, the right hand column in Figure 3 displays, purple lines, the best fitted functions obtained from linear combinations of the fitted functions employed for the pure components: blue lines for the undecanoic acid phase and red lines for the dodecanoic acid phase. The good agreement found between these fitted functions and the XRD experimental data, compared at left column

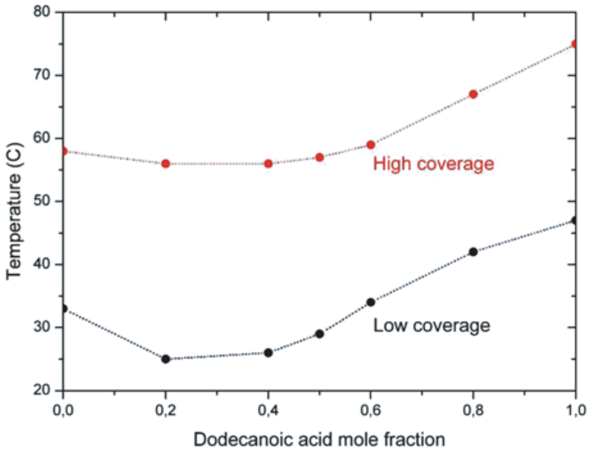

Fig. 4. XRD phase behaviour, monolayer melting point, as a function of bulk mixture composition, for the undecanoic acid – dodecanoic acid system adorbed onto graphite at submonolayer regime (black). Phase diagram from DSC measurements for the same system at high coverage (red), from Ref. [6], has been included for comparative purposes.

in Figure 3, allows us to conclude that the data are consistent with phase separation of the components in the solid monolayer for the studied composition range. If the mixed monolayers were mixing – i.e. an ideal solid solution – we should expect a simple linear displacement of the 2D peak position with composition and retaining essentially the same peak width as the pure component monolayers. Hence the fact that we observe a broadening of the monolayer peak also supports our tentative conclusion that these two components are phase separating in these mixed solid monolayers. However, for entropic reasons, the mixture of both phases in the monolayer at compositions close to the pure components could not be ruled out. Similar behaviour has been already observed in many other systems, such as rare gas mixtures monolayer adsorbed onto graphite [10].

The temperature dependence of the scattering patterns enables us to extract the composition dependence of the 2D melting phase transition, and a melting point for each composition – from the temperature at which the 2D peak disappears. Figure 4 illustrates the 2D melting temperature as a function of composition. This figure also includes previous results obtained for the undecanoic – dodecanoic system in the high coverage regime [5]. The diffraction data clearly indicate a significant depression in the monolayer melting point with composition. This is not what is expected on the basis of ideal mixing in the adsorbed layer but is much more typical of extensive non-ideal mixing and phase separation. This behaviour is similar to that previously reported for this system at high coverage. Hence we conclude again that the composition dependence of the monolayer melting transition is indicative of phase separation in both coverage regimes.

From a more quantitative point of view, we can consider the extent of the depression in the monolayer melting point compared to that expected if the two components mixed ideally in the monolayer. For both coverages, a depression of more than 10 °C and a displacement of the minimum in the monolayer melting point to the left side of the phase diagram is observed. The lowering of the 2D melting point in 2D mixtures has commonly been observed in other systems [11], and is in agreement with the variation of the 2D peak profile above mentioned. The displacement of the minimum is caused for the more favoured adsorption of dodecanoic acid onto graphite surface.

4 Conclusions

XRD measurements have been used to provide the phase separation behaviour, at submonolayer regime, of the monolayers of adsorbed binary mixtures composed of undecanoic and dodecanoic acids onto graphite. We conclude that these components essentially phase separate at all compositions on the surface and the scattering patterns of the binary mixtures are simply the linear sum of the diffraction patterns of the pure 2D crystalline structures. The phase separation is also reflected in the variation in the monolayer melting point with composition. This behaviour at sub-monolayer coverages also echos that observed previously at high coverages.

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