Neutron Diffraction from Benzene Adsorbed on Graphite

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Neutron diffraction has been used to determine the structural properties of benzene adsorbed on graphitized carbon black at coverages of 0.4 to 1.2 monolayers and temperatures from 100 to 200 K.

Benzene adsorbs on the basal planes of graphite to form a two-dimensional monolayer in which all the molecules lie flat, or very nearly so, with a molecular area of 37 Å². At low coverages and low temperatures the molecules aggregate in two-dimensional clusters rather than spreading over the surface to form a lattice gas.

Above a monolayer and at 100 K, any excess benzene in the system nucleates to form crystallites of normal orthorhombic benzene without disturbing the monolayer already present. There is therefore no structural phase change in the two-dimensional monolayer at higher coverages.

At 200 K the benzene forms a two-dimensional fluid at all the coverages studied. At low coverages the molecules in the fluid remain flat on the surface but at higher coverages they have greater orientational freedom.

There has long been argument about the configuration of benzene molecules adsorbed on the surface of graphite. Simple theoretical calculations of the intermolecular forces at the surface predict that an isolated molecule of benzene will lie flat on the basal planes that make up the surface of graphitized carbon blacks and exfoliated graphites.[1-4] On the other hand, the structure of the vapour phase dimer [5] and the crystalline solid [6, 7] suggest that interactions between benzene molecules will orient adjacent molecules perpendicular to one another. The most likely structure of a layer of benzene would then have all the molecules perpendicular to the surface. The balance of the opposing needs of surface–molecule and molecule–molecule forces will also be sensitive to changes in both coverage and temperature. Thus benzene might lie flat on the surface at low coverage but perpendicular at high coverage.

Early attempts to determine the benzene configuration by fitting statistical mechanical models to isotherms observed at relatively high temperatures gave contradictory results.[8-12] Khatir *et al.*[12] have recently measured isotherms at low temperatures and have observed rather peculiar behaviour which they interpret as follows. At low coverage all the benzene molecules are flat on the surface but, as the coverage increases, they gradually tilt away from the surface until they are all perpendicular to the surface at a limiting coverage. Boddenberg and Moreno [13, 14] have concluded from their interpretation of n.m.r. relaxation times that the molecules are all perpendicular to the surface at temperatures of 80-150 K. Stockmeyer and Stortnik [15] have also concluded that benzene molecules are perpendicular to the surface at room temperature, using neutron quasielastic scattering. In this paper we use the more direct technique of neutron diffraction [16, 17] to solve the problem.

EXPERIMENTAL

The adsorbent used was the graphitized carbon black, Vulcan III, with a specific area of 71 m² g⁻¹,[18] obtained from the National Physical Laboratory, Teddington. 5 g of adsorbent were outgassed in an aluminium container for 12 h at 300°C and 10^{-6} mmHg and the container mounted in a cryostat whose temperature could be varied from 77 to 300 K with an accuracy better than 1 K. A known volume of benzene vapour was introduced directly onto the adsorbent at room temperature, cooled slowly and extensively annealed. Diffraction patterns from different experiments were found to be completely reproducible.

For extra sensitivity in the neutron diffraction experiment fully deuterated benzene, obtained from Merck, Sharp and Dohme, was used in preference to C_6H_6.

Diffraction patterns were taken on the diffractometer D2 ($\lambda = 1.22$ Å) at the Institut Laue-Langevin.[19] After recording the background pattern of the adsorbent, the sample was not disturbed during deposition and annealing of the adsorbate. It was therefore possible to make extremely accurate (± 0.2 %) subtractions of the background. This was checked by comparing backgrounds taken after large variations in the temperature of the adsorbent.

RESULTS

Diffraction patterns [$^2H_6$] from benzene on Vulcan III at three different coverages and two temperatures are shown in fig. 1. The diffraction pattern of the adsorbent has been subtracted but, since the diffraction pattern of the adsorbent only has one reflection in this region, the (002) reflection from the basal planes of graphite at $2\theta = 20°$,
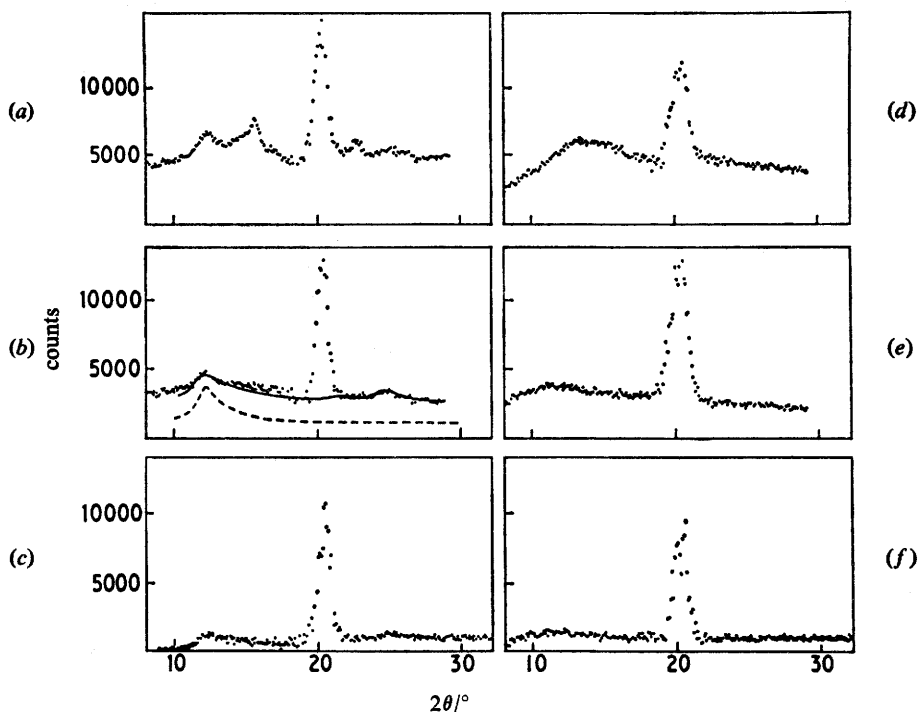

FIG. 1.—Neutron diffraction from benzene adsorbed on graphitized carbon black (Vulcan III). The background pattern from the Vulcan has been subtracted. The temperature and area of surface available per molecule are (a) 100 K, 30 Å²; (b) 100 K, 47 Å²; (c) 100 K, 95 Å²; (d) 200 K, 30 Å²; (e) 200 K, 47 Å²; (f) 200 K, 95 Å². The incident wavelength of the neutrons is 1.22 Å. The continuous line in (b) is the calculated diffraction pattern from a two dimensional layer with the structure shown in fig. 2. The dashed line in (b) is the pattern calculated for freely rotating benzene molecules in a hexagonal lattice of length 6.5 Å.

most of the features in the patterns of fig. 1 must result from diffraction from the adsorbed layer of benzene. The presence of an intense peak at $2\theta = 20°$, even after subtraction of the background, shows that the intensity of the (002) reflection of graphite is also affected strongly by adsorption of benzene.

INTERPRETATION

In the patterns at the two lowest coverages and at 100 K, there are two peaks at $2\theta = 12.5$ and $25.2°$ with shapes characteristic of reflections from a two dimensional layer [20] which we therefore index as (10) and (20) reflections from a two dimensional lattice of adsorbed benzene molecules. Both these coverages correspond with points on the isotherm well below the knee associated with completion of the monolayer and with areas available per molecule of 95 and 47 Å². The same two peaks are still present, but with slightly more intensity, at the highest coverage where the area available per molecule is down to 30 Å². However, at this higher coverage there are two new peaks with positions and intensities exactly as expected for bulk crystalline benzene. The exact nature of the " second adsorbed layer " is discussed further below but what is immediately apparent is that only a limited amount of benzene can be incorporated into the layer next to the surface. From the intensities of the diffraction peaks at the three coverages we estimate that the monolayer is complete when the area occupied per molecule is ≈ 40 Å².

The presence of only two reflections from the adsorbed monolayer shows that the two-dimensional lattice has high symmetry, probably hexagonal, or given that the reflections are rather broad, an oblique lattice, slightly distorted from hexagonal symmetry. In the range of angles observed there should also be a (11) reflection but this would be obscured by the (002) reflection from the graphite. The area occupied per molecule is 37 Å² which, if the molecules lay perfectly flat on the surface, would lead to a closest distance of approach of two hydrogen atoms of 2.4 Å which is not unreasonable.[21] The hexagonal symmetry of the two-dimensional lattice is consistent either with the molecules all lying flat on the surface or with them lying perpendicular to the surface but each one rotating more or less freely about an axis perpendicular to the surface. The latter is similar to the structure deduced from nuclear magnetic resonance.[13, 14]

If the factor dominant in determining the structure of the monolayer were the molecule–molecule rather than the surface–molecule interaction, we would expect the adsorbed layer to have a structure similar to the most dense lattice planes of bulk crystalline benzene. These are the (010), (111), (100) and (001) planes with areas per molecule of 25.8, 27.6, 33.5 and 35.7 Å², respectively. The high density of the (010) and (111) planes is achieved by packing adjacent molecules at right angles to one another. In the only plane with a density anywhere near as low as that of the adsorbed monolayer, the (001), benzene molecules are tilted at an angle of $\approx 45°$ to the plane. It is therefore probable that, if the benzene molecules are not free to rotate, they lie flat, or nearly so, on the surface. If the molecules are perpendicular to the surface but are rotating freely about an axis perpendicular to the surface the area occupied per molecule is also likely to be large.

The two possible conformations of adsorbed benzene can be distinguished by intensity and profile analysis of the observed peaks using the appropriate structure factors and Warren's formula for diffraction from two-dimensional layers.[20] For benzene lying flat on the surface the structural model shown in fig. 2 was used and gives excellent agreement between calculated and observed intensities as shown in fig. 1. The intensity calculated for the (11) reflection is low and this would make it

impossible to observe except possibly from an oriented adsorbent. The pattern calculated for benzene in a hexagonal lattice of similar spacing but with the molecules freely rotating about all axes is also shown in fig. 1. For reflections from the two dimensional layer this model will give similar intensities to those expected from the model proposed by Boddenberg and Moreno.[13, 14] It does not fit the observed pattern at all. Because of the large Debye–Waller factor associated with the rotational motion the (20) peak disappears.
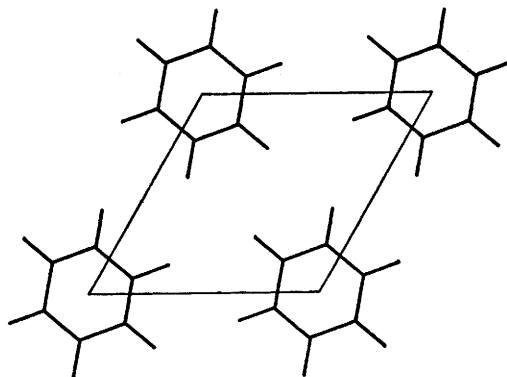

FIG. 2.—The arrangement of benzene molecules in the adsorbed layer. The hexagonal cell length is 6.5 Å.

The final evidence that benzene lies flat on the surface comes from the enhancement of the intensity of the graphite (002) reflection when benzene is adsorbed. The effect results from the interference of the scattering from the adsorbed layer with that from the basal planes of the graphite.[17, 22] A detailed analysis which will be presented in a later paper shows that the effect depends primarily on the structure factor of the adsorbed molecule perpendicular to the surface and is not sensitive to the model used to describe the shape of the diffraction peaks of the adsorbent itself. Absolute increases in intensity are difficult to calculate but, to establish the main conclusion of this paper, we need only consider the relative effects of adsorbed monolayers of krypton and benzene on the graphite (002) reflection. The calculations have been made for the two extreme cases of benzene lying flat on the surface or oriented perpendicular to it. Surface–molecule distances have been taken either from Steele [4] or estimated van der Waals radii and the surface density of benzene from the diffraction results of fig. 1. The enhancement of the (002) reflection by adsorbed krypton was measured in exactly the same way as for benzene using the same sample of Vulcan III. The relative enhancements of the (002) peak intensity are: benzene perpendicular/krypton, 0.1; benzene parallel/krypton, 4.2; observed, 4.8 ± 1.5. Clearly, benzene oriented perpendicular to the surface has little effect on the (002) reflection. The cause of the large enhancement when benzene is flat on the surface is mainly the much greater number of nuclei present in a single layer of benzene as compared with krypton (the scattering lengths of Kr, C and D are nearly the same). The intensity ratio for benzene lying flat is quite sensitive to the exact value chosen for the van der Waals radii and would also be effected by any tilt of the molecules away from being parallel to the surface. We estimate a maximum possible tilt away from the surface of 15°.

Although the main aim of these experiments has been to determine the configuration of adsorbed benzene at low temperatures, there are further results of interest. As the coverage is decreased well below a monolayer the structure remains the same,

showing that the molecules do not spread out evenly over the surface but form two dimensional clusters.

At coverages above a monolayer the diffraction patterns show no evidence of multilayer formation. Any benzene introduced to the system above a monolayer forms three-dimensional crystallites with the orthorhombic structure of bulk benzene. Similar behaviour has been observed for ammonia on graphite and has been shown to be associated with isotherms that cut the line $p/p_0 = 1.0$.[23] Khatir et al.[12] have shown that this also occurs in the adsorption isotherms of benzene on graphite at low temperatures. However, unlike the ammonia system, benzene first forms a mono-layer before any nucleation takes place. We have also observed diffraction patterns at temperatures between 100 and 200 K. By 200 K, at all three coverages shown in fig. 1, the first peak has broadened and the second vanished. The first peak also shifts to a lower angle, consistent with the molecules spreading over the surface to occupy the maximum possible area per molecule. Furthermore, since the intensity of the interference peak is still large, we conclude that the molecules are still lying flat on the surface. At the highest coverage shown in fig. 1 the area occupied per molecule decreases below 37 Å^2 at 200 K, suggesting that the molecules are tilting away from the surface so that excess benzene from the melting crystallites can be incorporated into the surface layer.

Our result, that benzene lies flat on the surface, does not agree either with the n.m.r. measurements of Boddenberg and Moreno[13, 14] or with the neutron quasielastic scattering measurements of Stockmeyer and Stortnik.[15] Stockmeyer and Stortnik's measurements were made at room temperature where it is certain that the thermal motion of the benzene molecules will prevent their lying flat on the surface. Indeed, the marked change in the isotherms is consistent with such a change in configuration. It is less easy to reconcile our results with those of Boddenberg and Morino which were made in the same temperature range. The n.m.r. experiment is less direct than a diffraction experiment and its interpretation therefore depends more on the choice of model. This is particularly true for surface experiments where there are a number of phenomena associated with T_1 minima that are not yet understood (see, for example, Tabony et al.[24]).

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