

## Oriented Adsorption of Benzene Molecules on Graphitized Carbon Black

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A new model for the oriented adsorption of benzene molecules on graphitized carbon black at low temperatures is proposed which explains NMR relaxation data.

Highly graphitized carbon blacks are known to possess energetically homogeneous surfaces as is well documented by numerous adsorption studies. This property is explainable with the notion that the faces of the polyhedral<sup>1</sup> particles are the graphite basal planes. There is much controversy in the literature about the structure and the dynamical state of the adsorption layer of molecules in the mono- and sub-monolayer regions<sup>1, 2</sup>.

The most controversial subject with this respect seems to be the system benzene/graphitized carbon black. Whereas Pierce and Ewing<sup>3</sup> conclude from adsorption isotherm and heat of adsorption measurements ( $-20$  to  $0^\circ\text{C}$ ) that localized adsorption is prevailing with the benzene molecules lying flat on the surface, Ross and Oliver<sup>1</sup>, on the other hand, were able to fit adsorption isotherms ( $0$  to  $50^\circ\text{C}$ ) with the assumption of two-dimensional real gas behaviour and free rotation of molecules about at least one axis. In view of the high anisotropy of the polarizability tensor of the benzene molecule the latter authors favour a model with the molecules standing up on the surface and rotating freely about the hexad axis. Steele<sup>2</sup> considers the molecules lying flat on the surface as the most probable orientation. The arguments of other authors<sup>4, 5</sup> are on similar lines. To our knowledge there is up to now no spectroscopic evidence in favour of one of these models. We were able to show from NMR measurements that neither of these models explains the low temperature ( $<150\text{ K}$ ) NMR data.

Using pulse NMR techniques the proton magnetic relaxation times  $T_1$  and  $T_2$  at 16 and 60 MHz have been measured of benzene adsorbed on Graphon

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- <sup>3</sup> C. Pierce and B. Ewing, *J. phys. Chem.* **71**, 3408 [1967].
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(Cabot Corp.) in the temperature range 280 to 80 K. The amounts adsorbed were 0.18, 0.36 and 0.72 mmol/g, which correspond to surface coverages  $\Theta = 0.5, 1$  and  $2$ , respectively, assuming  $40 \text{ \AA}^2$  to be the area occupied by one adsorbed molecule. In addition,  $T_1$  and  $T_2$  have been measured for  $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$ -mixtures at the same surface coverages in order to separate the intra- and intermolecular contributions to the relaxation rates. Using semiclassical NMR relaxation theory the following model is able to represent the measured  $T_1$  data ( $\Theta = 1$ ) for temperatures between 80 and 150 K within the range of experimental error.

- (i) The benzene molecules are adsorbed at fixed sites with their planes oriented perpendicularly to the graphite basal planes,
- (ii) the molecules perform reorientational jumps about diad axes to next positions  $\pm 60^\circ$  apart at a rate given by  $2.3 \cdot 10^{13} \exp(1060/T) \text{ s}^{-1}$ ,
- (iii) there is a two-dimensional ordered structure of benzene molecules with hexagonal symmetry. The distances of the centers of gravity of the molecules are determined by the graphite lattice.

Remarkably, with only slight deviations, the  $T_1$ -data are the same for surface coverages 0.5 to 2 which indicates that lateral interactions of the molecules are of importance. For  $\Theta = 2$ , a second phase of benzene was detected the  $T_1$  data of which are nearly equal to those of solid benzene as given by Haeberlen and Maier<sup>6</sup>.

The transversal relaxation function is temperature independent in the temperature range 80 to 150 K, but is of complex shape.

At temperatures above 150 K additional, presumably translational motions show up in the relaxation times. The interpretation of these data is being undertaken.

We are going on studying the adsorption of other molecules on graphitized carbon black and boron nitride by means of NMR pulse and low temperature adsorption techniques.

The full paper with the detailed results will be published in short.

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- <sup>5</sup> R. A. Pierotti and R. E. Smallwood, *J. Coll. Interf. Sci.* **22**, 469 [1966].
- <sup>6</sup> U. Haeberlen and G. Maier, *Z. Naturforsch.* **22 a**, 1236 [1967].