

12. *Studies in Adsorption. Part XII.*¹ *Mechanism of Adsorption of Aromatic Hydrocarbons by Chromatographic Alumina.*

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Naphthalene is adsorbed by chromatographic alumina from 2,2,4-trimethylpentane; 2,3-benzanthracene, phenanthrene, and pyrene, but not naphthalene, are adsorbed from xylene. Only a minute fraction of the available surface (*ca.* 0.1%) is covered. S-Shaped isotherms are obtained. It is suggested that a π -electron complex is formed between the hydrocarbon and a few sites, probably aluminium atoms, exposed by mechanical damage, on the outer surface of the oxide. The nature of the adsorption isotherms suggests that the hydrocarbon molecules are adsorbed in small clusters, in which they are stacked face-to-face edge-on to the oxide surface.

A PREVIOUS paper² described an investigation of the mechanism of adsorption of ionic and polar non-ionic solutes by chromatographic alumina. It was shown that the former are adsorbed mainly by an ion-exchange process and perhaps by covalent-bond salt formation, and the latter by hydrogen bonding (OH \cdots O; NH \cdots O; and CH \cdots O bonds were detected). Chelating compounds form complexes with the substrate.

Non-polar solutes were not studied. Alumina columns are, however, used for the separation of unsaturated hydrocarbons, which generally separate according to the length of their conjugate system or the number or coplanarity of the aromatic nuclei, those containing the longest system or the most nuclei being the less readily eluted.³⁻⁵ This appears to indicate that aromatic hydrocarbons are adsorbed on alumina, and therefore that some adsorption mechanism other than those detected for ionic and polar solutes is operating.

Basu⁶ suggested that this mechanism is one of molecular complex formation, facilitated by (a) a high electron affinity of one component and (b) a low ionisation potential of the other, and pointed out that, on the assumption that the energy of the top-filled orbital of a conjugated organic molecule calculated by the LCAO method gives a rough estimate of (b), the separations in two series of compounds (five condensed-ring aromatic hydrocarbons and four $\alpha\omega$ -diphenylpolyenes) agree in both cases with this hypothesis. In the previous paper² it was suggested that the mechanism might be either (a) formation of a complex between the π -electrons of the hydrocarbon and the alumina (a similar mechanism to that suggested by Basu) or (b) a partition effect, in which the rate of downward movement of solute is determined by the rate of its transfer from the initial solvent holding it at the top of the column to the eluting solvent. The present investigation was made to examine these suggestions.

While the present research was in progress Klemm *et al.*^{5a} reported an investigation of

¹ Part XI, Giles, MacEwan, Nakhwa, and Smith, *J.*, 1960, 3973.

² Cummings, Garven, Giles, Sneddon, and Stewart, *J.*, 1959, 535.

³ Williams, "An Introduction to Chromatography," Blackie and Son Ltd., London, 1946.

⁴ Strain, "Chromatographic Adsorption Analysis," Interscience Publishers Inc., New York, N.Y., 1942.

⁵ (a) Klemm, Reed, Miller, and Ho, *J. Org. Chem.*, 1959, **24**, 1468; (b) see other references in (a).

⁶ Basu, *Chem. and Ind.*, 1956, 764.

the adsorption of aromatic hydrocarbons on alumina from binary mixtures of various hydrocarbons, and judged the degree of separation of more than 40 pairs by effluent analysis. The ease of absorption appeared to be governed by three qualitative rules, being favoured by increase in the number of double bonds present in the solute, increase in the degree of its co-planarity, and by a "symmetry rule."

In the present work isotherms (Fig. 1) were determined for several aromatic hydrocarbons from two solvents on Grade II and Grade I alumina.

EXPERIMENTAL

Substrate.—This was chromatographic alumina Type H (Savory and Moore) (Grade II),² specific surface area, by phenol adsorption,² 5×10^5 cm.² g.⁻¹, used without further treatment, or after conversion into Grade I. This conversion was made by roasting the alumina in a muffle furnace at ca. 700° for 5 hr., with frequent stirring, and subsequent cooling *in vacuo*; the product was stored in a tightly sealed jar.

Effect of Dehydration of Substrate.—Roasting reduced the weight by 5.9%. Ignitions of alumina (corundum) up to ca. 400° result in very little loss of chemically bound water, the surface layer approximating to Al(OH)₃ being retained. At higher temperatures partial or complete dehydration, depending on the temperature, takes place to give a surface approximating to either AlO·OH or γ -Al₂O₃.⁷ In the present material, if the 5.9% loss on roasting is taken to be that of a monolayer of water molecules each occupying 8.2 Å² (the approximate cross-section, edge-on), it represents ca. 16×10^5 cm.² of extra surface per g. of powder, so that Grade I powder would on this assumption have 4.5 times the available active surface of Grade II. This figure agrees well with the 5.3-fold greater maximum adsorption of phenanthrene (Fig. 1, *a—c*) on Grade I than on Grade II powder. (An attempt was made to rehydrate Grade I to Grade II powder by storing it under moist air until it had increased 5.9% in weight, but there were experimental difficulties in stopping the increase at the correct value. The product had only ca. 60% of the phenanthrene-adsorbing capacity of the original Grade II powder; cf. Fig. 1*c*.)

Reagents.—The solutes were commercial products, purified by distillation or sublimation. The solvents were B.D.H. "Laboratory Reagent" grade 2,2,4-trimethylpentane ("Special for spectroscopy"), and xylene (mixed isomers) redistilled to b. p. range 138—142°. Even after distillation there appeared to be a trace of an impurity in the xylene which coloured Grade I alumina pale yellow. This was removed by shaking the solvent with charcoal and filtering. The impurity did not, however, appear to be adsorbed by Grade II alumina.

2,3-Benzanthracene is sparingly soluble, and solutions were prepared by leaving the solid in contact with the cold solvent for several days, and then filtering. All other solutions were freshly prepared just before use.

Adsorption and Analysis.—The hydrocarbons are adsorbed to a much smaller extent than the solutes previously used,² and the methods were accordingly modified to increase their sensitivity: 2 g. samples of alumina and 5 c.c. of test solution in ground-glass, stoppered tubes were shaken by hand for 10—15 min. at room temperature. (Preliminary rate tests showed that adsorption was complete in a few minutes.) The tubes were next set aside for 5 min. and a portion of each solution was then removed by decantation for spectrophotometric analysis, by the Unicam S.P. 500 instrument. Each result was obtained from the mean of 6—10 successive readings on each solution. This procedure occupied 30—60 min., and consequently, to ensure uniform treatment, each solution was treated separately with alumina immediately before analysis.

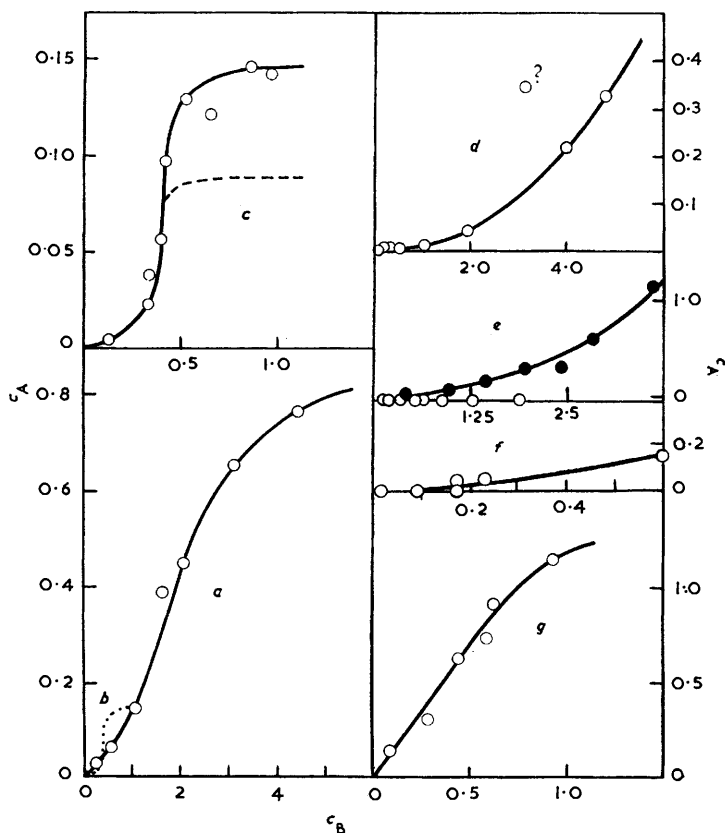
Phenanthrene was very little adsorbed, and to avoid possible inaccuracies caused by the necessary five-fold dilution of the test solutions for analysis at λ_{\max} , spectrophotometric readings on this solute were taken at a wavelength of *minimum* adsorption, at which the optical density is about one-fifth that at the maximum. All other solutes were determined at a wavelength of maximum absorption, if necessary after dilution with fresh solvent. 1 mm. or 10 mm. cells were used.

The isotherms for pyrene and 2,3-benzanthracene could not be taken as far as the plateau, because of the scarcity or the low solubility of the solutes.

⁷ O'Connor, Johansen, and Buchanan, *Trans. Faraday Soc.*, 1956, **52**, 229.

Tests with Cellulose, Graphite, and Silica.—Parallel tests with these substrates gave no evidence of adsorption of phenanthrene by cellulose (Whatman chromatographic powder) or silica (MSC powder¹), from benzene or xylene. The tests with graphite were inconclusive because a significant increase in optical density (at 3240 Å) of the solutions occurred. The increase was independent of solute concentration, and may have been caused by preferential adsorption of solvent.

FIG. 1. *Adsorption isotherms of aromatic hydrocarbons, etc., in xylene (except where indicated otherwise) on chromatographic alumina at 20°.*



c_A is the equilibrium concentration on the alumina (mmole/kg.) and c_B that in the bath (mmole/l.).
 (a) Phenanthrene (Grade I alumina). (b, c *) Phenanthrene (Grade II alumina); broken line shows isotherm from recycled Grade II (see Experimental section). (d) Pyrene (Grade II). (e) Naphthalene (Grade II) from 2,2,4-trimethylpentane; open circles show result of test with xylene solvent. (f) 2,3-Benzanthracene (Grade II). (g) Oxidation product of phenanthrene (Grade II).

* Curve c is repeated as b for comparison with a.

Adsorption of Phenanthrene Oxidation Product.—The optical density of phenanthrene solutions increased considerably on exposure to light for several days. The product was more readily adsorbed than unchanged phenanthrene and appeared to give an *L* isotherm, indicative of a polyfunctional solute oriented flat at the surface;¹ it may be biphenic acid (Fig. 1g).

RESULTS AND DISCUSSION

Mechanism of Adsorption.—Positive adsorption was detected with all the solutes except benzene in 2,2,4-trimethylpentane and naphthalene in xylene, and the rapidity of adsorption shows that it occurs only on the external surface of the particles. This agrees

with the evidence of Klemm *et al.*^{5a} that steady-state processes are occurring in the column, deduced from the applicability of the "law of inequalities," *i.e.*, if, amongst three hydrocarbons, A, B, and C, $A > B$ and $B > C$ in ease of adsorption, then also $A > C$.

Naphthalene is readily adsorbed from an aliphatic solvent, which presumably is itself unadsorbed. The non-adsorption of naphthalene from xylene must be the result of preferential adsorption of the aromatic solvent molecules at the very limited number of sites.

The amount of phenanthrene adsorbed is substantially higher on Grade I than on Grade II material, but the apparent affinity of phenanthrene is actually lower on Grade I than on Grade II (-3.7 and -5.1 kcal./mole respectively *).

The roasting treatment used to prepare Grade I material removes firmly bound water. Therefore, though Grade I oxide has higher affinity for water than Grade II, it has lower affinity for an aromatic hydrocarbon, but more available sites. This suggests that water and hydrocarbons are adsorbed at different sites. Water is probably hydrogen-bonded to oxygen, and it may screen some of the sites suitable for hydrocarbons. The absence of any adsorption by silica or cellulose (see p. 60) appears to show that neither oxygen atoms nor hydroxy-groups are sites for the hydrocarbons. Therefore the sites are probably aluminium atoms. The substrate is the γ -form of alumina, in which each aluminium atom is surrounded by six oxygen atoms, and is thus normally inaccessible to molecules adsorbed at the surface. The structure may, however, be distorted by abrasion in grinding. O'Connor *et al.*⁷ point out that, at a freshly fractured surface, co-ordination of some ions must be incomplete. They found that freshly ground corundum always had a positive zeta-potential in water, indicating the surface ionisation of hydroxyl groups, following extensive hydration of aluminium ions to give a layer of $\text{Al}(\text{OH})_3$. The hydrocarbons probably form a π -electron complex with the small proportion of aluminium atoms that happen to be exposed at the surface. Calculation from the position of the plateau in the phenanthrene isotherm shows in fact that only a very small fraction (*ca.* 0.06%) of the alumina surface is covered at saturation. Pyrene and 2,3-benzanthracene would clearly (see Fig. 1) cover rather more than this proportion, but still only a fraction of the total surface.

Klemm *et al.*^{5a} reached a similar conclusion, *viz.*, that the adsorption takes place on "active spots" of the alumina surface in a π -type (outer- or charge-transfer) complex; in addition they consider that the adsorption is unimolecular; also that it is flatwise, but the present results do not support the latter suggestion (see p. 62).

The following data, quoted by Basu,⁶ agree with the hypothesis, so also does the improved adsorption produced by (a) substitution of methyl or ethyl groups into aromatic hydrocarbon nuclei,^{5a} and (b) an increase in the number of methyl groups substituted in the benzene nucleus,^{5a} since these groups increase the electron availability in the nucleus.

Compound	Energy of topmost filled orbital	Position on Al_2O_3 column
Pentacene	0.205	Top
Tetracene	0.276	↓
Anthracene	0.379	
Naphthalene	0.535	Bottom
Benzene	0.800	
2,3-Benzanthracene	0.276	Top
1,2:6,7-Dibenzanthracene	0.500	Bottom

Water molecules must be attached very firmly to the oxygen atoms. This may increase the electropositivity of the neighbouring aluminium atoms, and so be responsible for the lower affinity of the surface for phenanthrene when water is removed to form

* Calculated from the expression, $-\Delta\mu^\circ = -RT \ln c$, where c is the solute concentration in a solution at equilibrium with alumina that has adsorbed half the maximum amount of solute. The value for pyrene on Grade II alumina is numerically less than -3.3 kcal./mole.

Grade I material. The donor molecule requires a low ionisation potential, and this is favoured by an increase in the length of its conjugate system.

The alumina-hydrocarbon bond here suggested may have some similarity to the complexes between benzene and silver cations⁸ and between the π -electrons of graphite and alkali-metal cations.⁹

Orientation of Adsorbed Hydrocarbon Molecules.—A recent investigation¹ into the relation between solution adsorption mechanisms and the shape of the resulting isotherms has shown that: (i) whenever the *S*-isotherm (*i.e.*, convex to solution-concentration axis)

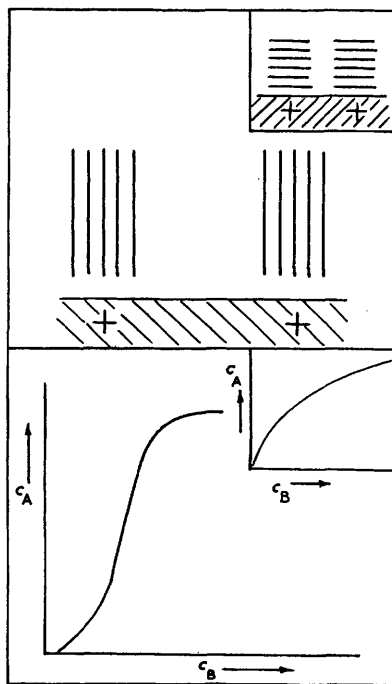


FIG. 2. Adsorption mechanism of aromatic hydrocarbons on alumina.

Top: Showing suggested stacking of isolated clusters of planar aromatic molecules (end-on) at Al^+ atoms exposed at the surface.

Bottom: Adsorption isotherm obtained, characteristic of end-on adsorption

Insets: Alternative stacking (not favoured) and corresponding isotherm.

is obtained, the most likely orientation of the adsorbed solute molecules is end-on to the surface, and in side-by-side association; (ii) when flatwise orientation occurs the normal isotherm (class "L," concave to solution-concentration axis) is always obtained; (iii) when further adsorbed layers very readily build up on the first, the curve rises steadily beyond the first inflection. All the present isotherms are of *S*-type; thus apparently the hydrocarbon molecules are adsorbed end-on, and not, as might at first sight appear most likely, flatwise. The surface coverage is extremely low, as already discussed, so the molecules appear to be stacked in small clusters at very isolated sites (Fig. 2). The reduction in adsorbability that follows substitution with alkyl groups larger than ethyl^{5a} is, on this hypothesis, the result of the steric hindrance of face-to-face packing.

Aromatic nuclei most readily associate face-to-face. Therefore flatwise adsorption would lead to the ready build-up of further layers on top of the first, and the isotherm would have a normal (concave) lower part, with an inflection followed by a steadily rising upper portion (*i.e.*, *L3a* type,¹ cf. Fig. 2, bottom, inset). (This type of curve has been observed for flatwise adsorption of layers of a merocyanine dye on silver halide, see Fig. 6a, ref. 1.)

⁸ Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801; Smith and Randle, *J. Amer. Chem. Soc.*, 1958, **80**, 5075.

⁹ Croft, *Quart. Rev.*, 1960, **14** 1.

Part XI, Errata.—In Table 1; *S* curves, entry for phenol, *S1* isotherm, *for* ref. *2a* *read* ref. *12a*; *L* curves, entry for phenylazo-2-naphthol, *L2* isotherm, *for* ref. *12a* *read* ref. *14*; *C* curves, entry for azobenzene, *for* isotherm *C1* *read* *C1(?)*; footnote ¶ *should read* ref. *12b*.
p. 3390, line 13, *for* refs. 7,5 *read* ref. 15.

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