Table 1. SPECIFIC SURFACE OF GRAPHITIC ACID DETERMINED WITH POLAR MOLECULES

Sorbed molecule	Molecule S (Å²)	Technique	Temperature	g/g GA	V_m (cc/g)	Specific surface (m²/g)	dGA	Type of complex
Water	10·8	B.E.T.	20° C		102	298 × 2	9·2	α
Ammonia*	15	B.E.T.	−47° C		147·5	592 × 2	9·2	α
Ammonia*	15	B.E.T.	0° C		154	619 × 2	9·2	α
Ammonia†	15	B.E.T.	0° C		207·4	833 × 2	9·2	α
Acetone	25	B.E.T.	20° C		89·5	550 × 2	9·0	α
Ethylene glycol	33	Joly balance	room temperature	0·2558		1,650	9·06, 9·6 (ref. 2)	α
n-Butylamine	20 ?	B.E.T.	20° C		136		14·97	β
n-Octanol	20 ?	Joly balance	room temperature	0·791			23·5	β

* Samples oxidized once.
† Samples oxidized three times.
S = Surface; V_m = volume of vapour for monolayer; dGA = (001) spacing of graphitic acid in Å.

The following molecules were sorbed: water, ammonia, acetone, ethylene glycol, n-butylamine and n-octanol.

The experimental results are shown in Table 1. The specific surface of the graphitic acid was calculated according to the formula C_4O_2H of molecular weight 81·05, leading to a value of 1,550 m²/g.

With water, ammonia, acetone and ethylene glycol, the sorbed molecules lie with their axes parallel to the surface of the lamellae giving an α complex[2].

The measurement of the surface in this case presents no difficulty, and with ethylene glycol a value is obtained for the total surface ($S_{int} + S_{ext}$).

The problem is more complicated if one tries to make a quantitative study of the β-complexes. In these, the molecules are more or less perpendicular to the layer, although some of the terminal carbon atoms may be in contact with the layer[3,4].

The completely erect position of the molecular chain is a limiting case, which is favoured by low temperatures[5].

Thus, the surface covered by butylamine and octanol cannot be calculated until the configuration of these molecules in the sorbed state is known. A calculation of the number of Å² corresponding to each molecule of octanol results in a value of 42 Å² (for specific surface 1,550 m²/g). A calculation of the density of the interlamellar liquid (using the X-ray value of the interlamellar spacing) gives $d_{20°}$ = 0·54. The sorbed layer is thus much less dense than the liquid ($d_{20°}$ = 0·84).

We intend to make further investigation of the density and heat of sorption of polar molecules with graphitic acid.

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Formation of Mercuric Iodo-acetate in Glacial Acetic Acid and its Reactions with Olefines

THERE are many examples in the literature referring to mercury salts of the type $Hg.R_1.R_2$, where R_1 and R_2 are different anions. In aqueous solution it has been shown by Raman spectroscopy that a mixture of mercuric chloride and bromide gives rise to the molecule HgCl.Br (ref. 1), while HgClI exists in the gas phase[2]. Molecular weight and conductance measurements of a mercuric bromide solution of mercuric sulphide indicates, however, that $2HgS.HgBr_2$ is formed[3].

The red polymorphic form of mercuric iodide is sparingly soluble in hot glacial acetic acid but dissolves readily in a solution containing mercuric acetate such that one mole of mercuric acetate just dissolves one mole of mercuric iodide[4]. On cooling the solution yellow needle-like crystals are obtained which, on standing for a few hours, turn red with separation of mercuric acetate. The driving force for solution is the formation of Hg(OAc)I or HgI_2. $Hg(Ac)_2$. To distinguish which of these hetero-anion salts may be formed an ebullioscopic determination of molecular weights was carried out using a conventional all-glass Cotrell pump apparatus. It has been suggested that mercuric acetate in aqueous solution probably consists of indefinitely long chains[5]. Using A.R. glacial acetic acid throughout, recrystallized mercuricac etate and resublimed mercuric iodide, the apparatus was calibrated using triphenyl methane. Over the concentration range 0·025–0·1 M, mercuric acetate was found to be monomeric (found, 335, 330, 324, 312; calculated, 318·7). Recently the molecular weights of mercuric halides in acetone were measured and indicated that they are monomeric in this solution[6]. The observed elevations over a similar concentration range, but containing mercuric iodide, indicated that monomeric Hg(Ac)I was formed (found, 346, 370, 376, 382; calculated, 386·6).

In order to assess the consequences of forming a hetero-anion salt the reaction of mercuric iodo-acetate with olefines was studied. Hugel and Hibou[7] investigated the olefine complexes formed by mercuric acetate and noted that mercuric iodo-acetate does not react directly with 1,2-hexadecene to give $C_{16}H_{32}Hg(Ac)I$. Ethylene was passed into a refluxing solution of mercuric iodo-acetate (3·87 g). After 3 h, mercuric iodide was obtained unchanged from the solution (2·20 g) and the complex $C_2H_4.Hg(OAc)_2$ recovered after evaporation of acetic acid ($C_8H_{10}O_4Hg$ requires C, 14·9 per cent; H, 2·0 per cent—found, C, 14·1 per cent; H, 2·1 per cent). The reaction with 1-dodecene led to quite different products. From a reaction mixture of mercuric iodo-acetate (30·8 g) and 1-dodecene (13·6 g) in refluxing glacial acetic acid mercurous iodide was obtained (9·92 g). On cooling, mercuric iodide (3·36 g) was obtained and, after removal of acetic acid, a heavy unstable oil. Vacuum distillation resulted in the formation of large drops of free mercury; gas chromatographic analysis showed that the distillate consisted of dodecene and two other high boiling products neither of which contained iodine. The resolution of this mixture is the subject of further work.

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