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Adsorption Isotherms of Carbon Dioxide at 273°K on Adsorbent Carbons & Evaluation of Microporosity using Dubinin Equation

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Adsorption isotherms of carbon dioxide (273°K) at low pressures up to about 200 torr on a variety of adsorbent carbons are reported. The slope of the linear Dubinin plot gives a measure of the adsorbate-adsorbent interaction while the intercept gives a measure of microporosity or effective surface area of the adsorbent. The values are in fair agreement with those obtained from BET technique based on low temperature (78°K) adsorption of nitrogen. The degassing of charcoal at 600° causes a considerable rise while that of carbon blacks causes a slight fall in microporosity. The degassing of each at 1000° causes a fall in microporosity, more so in charcoal than in carbon blacks.

SEVERAL investigations on the adsorption of carbon dioxide by microcrystalline carbons¹⁻⁷ at temperatures around 273°K and comparatively low pressures up to 200 torr have been reported and data have been used for estimating microporosity or conventional surface area by applying Dubinin equation⁸. The widely used BET method has been criticized and has been shown to provide a measure of total internal volume in micro- and transitional pores and not of microporosity⁹. It was thought of interest to study adsorption of carbon dioxide at 273°K and pressures approaching 200 torr on a series of adsorbent carbons in order to check the applicability of Dubinin equation and to compare specific surface area values obtained by this technique with those obtained by the conventional BET technique. It may also be of interest to know the effect of degassing on surface areas of these materials.

Charcoal, prepared by the carbonization of cane sugar¹⁰, a few samples of carbon blacks including Graphon (a highly graphitized material received as gift from Cabot Corporation, USA) and five commercially available activated carbons were used. Adsorption of carbon dioxide was studied volumetri-

well known BET apparatus. Carbon (0.2 g oven-dried at 120°) was taken for each experiment. The pressure range studied varied from ~2 to ~200 torr. Equilibrium was attained within 1 hr at each pressure. The saturation pressure (p_s) of carbon dioxide (purity 99.8%) at 273°K was taken as 34.4 atmospheres.

In accordance with Dubinin equation (1)

$$\log V = \log V_0 - D (\log p_s/p)^2 \quad \dots(1)$$

(where V is volume of carbon dioxide adsorbed at equilibrium pressure p , V_0 is micropore capacity, p_s = saturation pressure of the gas and $D = 2.303 kR^2T^2/\beta^2$ where β is the affinity coefficient of the adsorbate and k is a constant). The plots of $(\log p_s/p)^2$ against $\log V$ for a number of carbon blacks and sugar charcoals were linear. The slope of the linear plot gives the value of D while the intercept at $(\log p_s/p)^2 = 0$ provides the value of V_0 , taken as a measure of microporosity, or as a measure of effective surface area⁸. Taking 17 \AA^2 as molecular area of carbon dioxide at 273°K (ref. 7), microporosity can be converted into conventional surface area which is accessible to CO_2 molecules through pore entrances of width $>4.2 \text{ \AA}$ which is molecular thickness of CO_2 . Since D is inversely proportional to β^2 , a higher value of D , evidently, indicates smaller adsorbate-adsorbent affinity. It appears, therefore, that the adsorbate has a greater attractive interaction with the first 9 carbon blacks than with the activated carbons. This is in conformity with the observations of Lamond and Marsh⁶ who found the value of D to rise, and therefore, the affinity to fall, on activating polyfurfuryl alcohol carbon to increasing burn offs. Walker *et al.*^{7,11} also found the value of D to be higher in activated carbons than in carbon molecular sieve materials. In activated carbons, the pores are relatively wider and hence the number of pore walls per g is smaller. The adsorbate interaction is, therefore, relatively smaller. The values of D in the case of Graphon, Kosmos 40 and Philblack A, which are essentially non-porous, are appreciably higher. The adsorbate interaction is very low due to virtual absence of pore walls.

The specific surface area values as obtained by the conventional BET technique based on low temperature (78°K) adsorption of nitrogen are also included in Table 1 for the sake of comparison. Considering the differences of approach in the two methods the agreement in the values obtained may be taken as fairly satisfactory. In any case, the objection to the use of conventional BET technique on the ground of condensation of nitrogen in pores⁹ does not appear to be valid as the value of surface area obtained by this technique then would have been much higher. However, there are distinct advantages in using carbon dioxide since it is a readily available and 273°K is the temperature which can easily be maintained.

The effect of degassing sugar charcoal and some of the carbon blacks on their surface area, about which very little information is available in the literature, is shown in Table 2. It is seen, in the first instance, that degassing of sugar charcoal at

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TABLE 1 — *D* VALUES (FROM EQ. 1) AND SURFACE AREAS OF VARIOUS CARBONS OBTAINED BY TWO METHODS

Carbon	<i>D</i> × 10 ⁻³ (Eq. 1)	Surface area (m ² /g)	
		From Dubinin plots	From BET (N ₂) method (ref. 15)
Mogul	14.09	324	308
Mogul A	14.00	252	228
ELF-0	14.61	209	171
Spheron-4	15.09	224	153
Spheron-6	15.58	138	120
Spheron-9	14.76	151	115
Spheron-C	15.65	288	254
Philblack-I	15.95	103	117
Philblack-E	17.80	132	135
Philblack-A	24.39	46	46
Graphon	25.00	91	76
Kosmbs-40	19.01	33	31
Sugar charcoal	14.31	338	337*
<i>Activated carbons</i>			
A	18.01	1148	1093*
B	18.72	1005	987*
C	19.83	955	821*
D	18.98	794	738*
E	19.81	550	505*

*Values obtained in the laboratories of Fertilizer Corporation of India, Sindri, for which the authors are thankful to Shri V. K. Puri.

 TABLE 2 — EFFECT OF DEGASSING CHARCOAL AND A FEW CARBON BLACKS ON *D* AND SURFACE AREA VALUES AS OBTAINED FROM DUBININ PLOTS

Carbon	Degassed at 600°		Degassed at 1000°	
	<i>D</i> × 10 ⁻²	Surface area (m ² /g)	<i>D</i> × 10 ⁻²	Surface area (m ² /g)
Sugar charcoal	17.56	660	17.52	323
Mogul-A	14.58	240	14.74	182
Mogul	14.23	295	15.28	239
ELF-0	14.73	189	15.45	166
Spheron-4	15.43	192	15.72	130

600°, which is known to cause elimination of tarry matter as well as combined oxygen capable of evolving carbon dioxide¹², causes a considerable rise in surface area, evidently due to availability of additional space previously blocked by these species. The adsorbate interaction, however, decreases as indicated by the rise in value of *D*, due to widening of capillary pores. The same treatment when extended to carbon blacks, on the other hand, causes a slight fall in surface area. These blacks are essentially free of tarry matter but they do contain 0.6 to 2.2% oxygen which comes off as carbon dioxide on degassing at 600° (ref. 13). It appears that this oxygen, in the case of carbon blacks, is not present within the micropores. This view is also supported by the fact that there is no significant rise in the value of *D* in the case of carbon blacks.

The appreciable fall in surface area on degassing sugar charcoal as well as each of the carbon blacks at 1000° appears to be due to shrinkage in pore structure as has been observed by Toda *et al.*¹⁴ in the case of coals.

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Viscosity of Cesium Chloride in Ethylene Glycol

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The viscosities of cesium chloride solutions in ethylene glycol at concentrations varying from $6.8 \times 10^{-3}M$ to saturation and at temperatures 25°, 30° and 40° are reported. The results are interpreted in terms of structure breaking capacity of the electrolyte by evaluating the temperature coefficient of constant-*B* of the Jones-Dole equation. The activation energy of the viscous flow is calculated from the Arrhenius equation.

It has been found by number of workers¹ that the addition of an electrolyte could either break or make the structure of a liquid. Since viscosity is a property of liquids which depends on the intermolecular forces, the structural aspects of liquids can be inferred from the viscosity of solutions at different concentrations and temperatures. With the development of the interionic theory, much of the interest in the subject has been directed towards accurate determination of the viscosities of very dilute solutions of electrolytes and the theoretical interpretation of the results. The aim of the present study is to determine the viscosity of solutions of cesium chloride in ethylene glycol at different temperatures and concentrations of the electrolyte and to analyse the data in terms of Jones-Dole equation² (1)

$$\eta/\eta_0 = 1 + AC^{1/2} + BC \quad \dots(1)$$

where *C* is the molar concentration and *A* and *B* are the constants representing the contribution from interionic electrostatic forces³ and ion-solvent interaction respectively. Structure breaking capacity of the electrolyte and effect of temperature on the coefficient *B* have also been studied.