An Estimation of the Degree of Surface Homogeneity of Carbons

by

D.K. Suri, P.T. John and K.C. Nagpal
Materials Characterization Division
National Physical Laboratory
New Delhi-110012, INDIA
Present address: 749, J.N.U. Quarters
New Campus, New Delhi-110067, India.

Abstract. It has been shown that with heating of carbons the degree of homogeneity increases as evident by the step formation of the John's isotherm plots. With homogeneity the crossing of the isotherms at two neighbouring temperatures shifts to a lower relative pressure corresponding to that of monolayer capacity.

INTRODUCTION

A surface is said to be heterogeneous when sites on a surface have different potential energy. Halsey[1] observed that when a nonporous surface is nearly homogeneous the isotherm should assume a step-like form. According to him a multilayer isotherm based on the hypothesis $E_1 > E_2 > ---- > E_i$ must lead to an isotherm composed of series of steps where E_i refers to the heat of adsorption of the ith layer. Gregg and Sing[2] stated that the sharpness of steps depends on ϕ/kT where ϕ is the interaction energy and it decreases with thickness of layer and temperature. Hence as ϕ decreases and as T increases the sharpness becomes less. It is observed that interaction energy is more for a gas which has got higher polarisability. Ponec et al[3] stated that physical adsorption theory demands distinct discontinuities in isotherm with phase transitions. Phase transition becomes more distinct with more homogeneity of carbon black in course of graphitization. It was shown earlier[4] that John's adsorption isotherm clearly shows phase transitions and inhomogeneity in pore size distributions by means of kinks or discontinuities in the isotherms. The purpose of this paper is to show that the isotherm can be used to find the sharpness of step-like isotherms, monolayer capacity and to determine a measure of degree of homogeneity.

METHOD

It may be stated that John's isotherm can be expressed in terms of pressure or relative pressure.[4] The isotherm expressed in terms of pressure is

$$\log \log p = C_o + n_o \log v \qquad (1)$$

and that in terms of relative pressure is

$$\log \log P = C + n \log v \qquad (2)$$

where $P = (p/p_s) \cdot 10^N$ and N is an integer between 2 and 6. The meaning of symbols were given earlier in several papers.[4-8] It may be stated that C, C_o, n and n_o are constants. Published data[2,9] were used to test the method. Using the data taken from reference 2 (Fig. 2.21(a)- Krypton on Carbon black at 90K; Fig. 2.21(b)-Krypton on Cadmium bromide at 73.1K and Fig. 2.24-Argon on Spheron - 6 carbon black at 78K heated to various temperatures), graphs were drawn between log log P and log v or between log log p and log v depending on whether the amount adsorbed is given in terms of relative pressure or pressure. The graphs gave straight lines representing different phases of adsorption (submonolayer, multilayer, capillary condensation, micropore filling etc.) with kinks or discontinuities at the point of phase transitions. As graphitization and/or homogeneity increased the step-like formation appeared more and more distinctly. In all these cases the amount adsorbed at the first step or kink (monolayer capacity) are given in Table 1. Similar graphs were

Table 1. Amount Adsorbed at Monolayer

System	Temp (K)	Heating Temp. (C)	Monolayer Capacity (cc) Cal.	Pub.
C.black - Kr	90	2700	3.31	3.53
$CdBr_2$ - Kr	73.1	-	0.13	0.14
Spheron 6-Ar	78	1000	27.23	24.48+
-do-	78	1500	26.30	23.64+
-do-	78	2000	25.70	22.95+
-do-	78	2700	24.89	22.60+

+B-point value since BET curve is non-linear.

drawn using data of reference 9 (Nitrogen on graphitized carbon black at various burn off at 77K and 90K). Each graph consisted of two isotherms of two neighbouring temperatures 77K and 90K. These graphs also showed straight lines with kinks. The surface area corresponding to the amount adsorbed at the first kinks (monolayer capacities) are given in Table 2.

Table 2. Surface Area Adsorbed at Monolayer Capacity.

Burn Off (%)	Surface Area (m^2/g) from Monolayer at 77K	Monolayer at 90K	Crossing Volume	Measure of Homogeneity
0.0	65.8	63.2	66.2	1.7
9.3	79.6	76.2	88.8	10.9
24.6	97.9	93.0	110.5	15.0
52.8	120.4	114.4	153.0	35.6

+System of adsorption isotherm is graphitized carbon black - Nitrogen.

DISCUSSION

Stepwise isotherm is due to the decrease in binding energy of layers (which falls of rapidly) with distance to substrate. This is one of the reasons why the higher layer steps become blurred. An additional factor tending to obscure steps even on a uniform surface is thermal excitation between adjacent layers. This happens because kT becomes comparable to or larger than the difference in their binding energies to substrate.[2] The most uniform films are those which display the greatest number of steps.

The graphs using the data from reference 2 gave step-like isotherms. It was observed that the volume adsorbed at the first step is identical to monolayer capacity. It is evident from Table 1 that in the case of the adsorption of argon on Spheron 6 the monolayer capacity values decreases with heating. It can be stated that the kink of John's isotherms at lower homogeneity transforms into a step as graphitization and/or homogeneity increases. It was observed that John's isotherms of two neighbouring temperatures drawn using data of reference 13 cross at some point above pressure corresponding to monolayer.[10] A measure of homogeneity is calculated as the difference between equivalent surface area corresponding to crossing volume and the mean of surface area from monolayer at two neighbouring temperatures and is given in Table 2. Less the above difference more the homogeneity. When graphitization and/or homogeneity is maximum the crossing point almost becomes identical to monolayer point. It appears that with graphitization and/or homogeneity the angle between straight lines representing different phases of adsorption becomes less obtuse and finally becomes right angle with maximum graphitization and/or homogeneity. It agrees with the fact that phase transition becomes more distinct with more homogeneity and/or graphitization. Crossing of isotherms means that the amount adsorbed after crossing is more at higher temperature than at lower temperature. According to Lopez-Gonsalez et al[11] this behaviour can be attributed to change in condition of adsorbate film in the vicinity of monolayer. There is a localised adsorption at preferred lattice position giving an ordered solid-like structure so that an increase in temperature leads to an increase in disorder allowing additional adsorption on surface layer.

CONCLUSION

With increase in homogeneity John's adsorption isotherms show sharper step-like formation. Each step corresponds to completion of a layer. The amount adsorbed at first step is identical to monolayer capacity. As homogeneity increases the volume corresponding to the crossing of isotherms at two neighbouring temperatures come closer to volume corresponding to monolayer. The degree of homogeneity is inversely proportional to the difference between the amounts adsorbed at crossing and monolayer capacity. When homogeneity is maximum, the volume adsorbed at crossing point is equal to monolayer capacity.

REFERENCES

1. G.Halsey, J. Chem. Phys., 16, 931(1948)
2. S.J.Gregg and K.S.W.Sing, Adsorption, surface area and porosity, Academic Press, London(1982).
3. Y.Ponec, Z.Knor and S.Cerny, Adsorption on Solids, Butterworths, London(1974).
4. P.T. John, D.K.Suri, K.C.Nagpal and T.A.K.Ghori, J. Scient. Ind. Res., 40, 371 (1981).
5. P.T.John, D.K.Suri and K.C.Nagpal, Carbon, 20, 67(1982).
6. P.T.John, Carbon 22,(1984), in press.
7. P.T.John, D.K.Suri and K.C.Nagpal, Carbon, 22,(1984), in press.
8. P.T.John, D.K.Suri and K.C.Nagpal, J. Materials Science,(1985), in press.
9. J.deD. Lopez-Gonsalez, F.Rodriguez-Reinoso and C.Salnas, Proc. 14th Biennial Conference on Carbon, (Pennsylvania State University, USA)(1979), p. 171.
10. P.T.John, Indian J. Technol. in press.
11. J.deD. Lopez-Gonsalez and F.Rodriguez-Reinoso, Adsorption at the gas-solid and liquid-solid interface, Ed. by R. Rouquerol and K.S.W.Sing, Elsevier Scientific Publishing Co.,New York(1982).