

Surface Area and Micropore Volume Measurements of Spherocarb and Sucrose Char

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Spherocarb와 Sucrose Char에 대한 비표면적과 세공부피의 측정

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Abstract: The amount of nitrogen gas adsorbed by Spherocarb and Sucrose Char was measured as a function of the relative pressure with temperature being kept constant at 77 to 184K. Isotherms at different temperatures were obtained by keeping the adsorbent at a constant temperature using liquid nitrogen, iso-pentane, n-pentane, ethyl alcohol, and iso-propyl alcohol slush baths. The objective for this study is to provide information on the specific surface area and pore volume by analyzing the experimental data using adsorption models such as the Brunauer-Emmett-Teller and Dubinin-Radushkevich models.

요 약 : Spherocarb와 Sucrose Char에 의해 흡착된 질소가스의 양은 온도를 77K에서 184K까지 일정하게 유지시키면서, 상대적 압력의 함수로서 측정되었다. 다른 온도에서의 Isotherm은 흡착제를 일정한 온도에서 유지시키면서, 액화질소, iso-펜탄, n-펜탄, 에틸알코올과 iso-프로필 알코올의 Slush bath를 사용하여 얻어졌다. 이 연구의 목적은 BET와 D-R 같은 흡착모델을 사용하여, 실험적 데이터를 분석함으로써, 비표면적과 세공부피에 대한 정보를 얻는데 있다.

1. Introduction

Many manufactured carbons contain pores which result from the manufacturing process (i.e., activation) or are inherent in the microstructure of the raw materials. The porosity is the most impor-

tant constituent of the porous structure of solid adsorbent, such as activated carbon. The presence of pores in a carbonaceous material will have a significant influence upon important properties such as density and surface area. Also, pores can act as sites for adsorption.

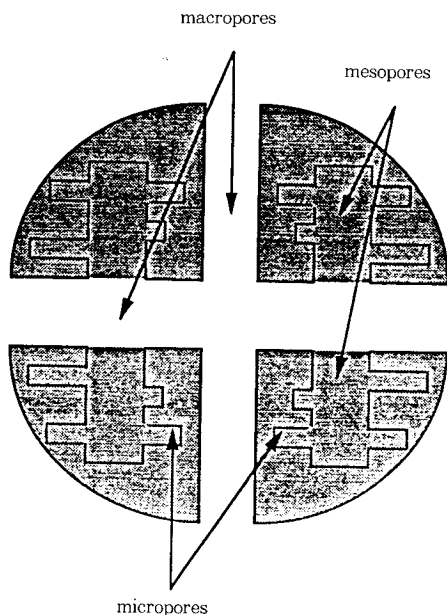


Fig. 1. Pore tree structure for the different types of pores.

McEnaney and Mays[1] reported that electrical and thermal conductivities decrease with increasing porosity since a reduced amount of solid is available to conduct electrons and heat. They also found that pores have a significant effect upon gasification reactions, at temperatures where diffusion of reactant and product gases in the pores affects the rate. The pore systems of carbons are of many different kinds. The individual pores may vary largely both in size and in shape within a given carbon. Dubinin [2] originally proposed a classification of pores according to their average width.

Fig. 1 gives a schematic representation of the different types of pores in a porous carbon. The macropores of a porous carbon serve as transport pores which let the molecules of the adsorptive reach the smaller pores, as shown in Fig. 1. Since the surface area of macropores is very low, the macropores are not significant from the point of view of the amount adsorbed on them, but the macropores influence the rate of admission of the

adsorptive by the carbon.

Based upon the pore tree structure, the mesopores which branch off from the macropores act as passages to the micropores for the adsorptive. In the mesopores, capillary condensation with the formation of a meniscus of the liquid adsorbate can take place. The surface area of mesopores is higher than that of macropores, but lower than that of micropores. The mesopores can be produced by enlargement of micropores.

In the micropores, most of the adsorption takes place, and the interaction potential is significantly higher than in mesopores or macropores. Their size prevents capillary condensation which occurs since the saturation vapor pressure is reduced by the effect of the interaction potential and the amount adsorbed at low relative pressures is enhanced. According to Rodriguez-Reinoso and Linares-Solano [3], at least 90~95 % of the total surface area of an activated carbon correspond to micropores. It is known that the porous structure of an activated carbon is a function of the precursor which is used in its preparation, the activation process, and the extent of activation. For this reason, the surface area and pore volume of activated carbons can vary widely from one to another. In this study, we have undertaken to examine the properties of different microporous carbons used as adsorbents. The surface area and pore volume of an adsorbent are fundamental properties, which are related to adsorption capacity.

2. Experimental

A volumetric adsorption apparatus[4] which is designed to enable us to measure the pressure, temperature, and gas sample volume before and after contact with the adsorbent was used to collect adsorption data. This apparatus is mounted inside a double-walled plywood box and a plexiglass door. Fiberglass insulation was placed in the wall space in order to maintain the entire system as isothermal as possible. The temperature in the box is monitored

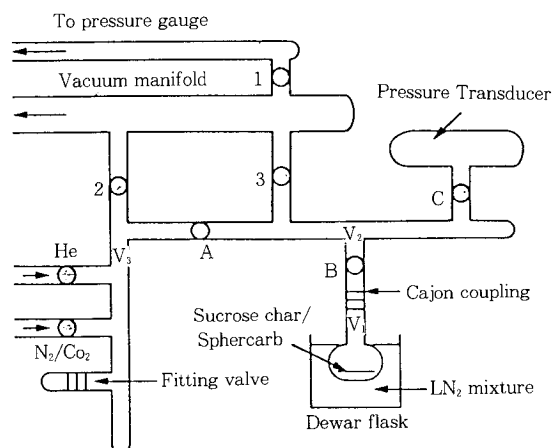


Fig. 2. Volumetric adsorption apparatus.

using a mercury thermometer which is accurate to within $\pm 0.1^\circ\text{C}$. The box is also equipped with a fan in order to cool the entire system. As shown in Fig. 2, A, B, C and 1, 2, 3 indicate high vacuum stopcocks equipped with Viton O-rings on the shank and tip, and rated at a static leak of less than 10^{-9} cc atm/sec. The gas storage volume, V_3 , is supplied with helium or nitrogen gas, through two gas tanks via a pressure regulator which can be read 0–10 psig. Matheson UHP grade helium and nitrogen gas metered by the high purity regulator were used in the experiments. The inlet valves, which control the gas entering into the system, are connected to V_3 . Directly above V_3 is a valve leading to the vacuum manifold. Near the bottom of V_3 is a fitting valve which controls the air entering the apparatus. To the right of V_3 is a valve leading to the working volume, V_2 , with a Cajon Ultra-torr connector. This V_2 leads to three different valves, in addition to a connection to V_3 . Two valve ports are on the top of V_2 . One of these ports leads to the 25mm ID vacuum manifold, and the other one leads to the MKS 220B™ absolute pressure transducer, which gives a voltage signal proportional to the pressure. The signal is read using a Fluke digital multimeter.

Spherochar and Sucrose Char, which are microporous carbons, were prepared for samples in these experiments. Spherochar was bought from

Table 1. Elemental Analysis for Sucrose Char and Spherochar

Composition	Sucrose Char	Spherochar
C (wt %)	95.9	96.8
H (wt %)	1.08	0.73
O (wt %)	3.02	2.43
Ash (ppm)	—	200

Analabs, North Haven, Connecticut. The other char used in these experiments was prepared by pyrolysis of Sucrose. Sucrose Char was manufactured by pyrolyzing small quantities of reagent grade Sucrose under nitrogen, 99 percent pure. Sucrose crystals were placed in a porcelain boat in the middle of the tube and initially heated to 800°C over a period of 10 minutes at a rate of $45^\circ\text{C}/\text{min}$. The temperature was kept at 800°C until all the volatile materials were dried out. The elemental analysis for Spherochar and Sucrose Char is summarized in Table 1 [5, 13].

Prior to the determination of an adsorption isotherm, the sample must be outgassed at an elevated temperature in order to remove any physically adsorbed material from the surface of the adsorbent. The outgassing was conducted by exposing the solid to high vacuum at elevated temperature.

The experiment was performed as follows: we turned on the 60 W-heating mantle under the sample bulb and plugged it into a variac at 80V. This resulted in heating the sample to 160°C . The sample was outgassed for several hours at this temperature and a nominal system vacuum of 10^{-4} – 10^{-5} torr for removal of any physically adsorbed material from the micropores.

Liquid nitrogen bath provided the 77K isotherm in this experiment. Other baths were used to obtain other adsorption isotherms. A slush bath is a coolant consisting of a low melting liquid which has been partially frozen by mixing with liquid nitrogen. This bath is prepared by pouring liquid nitrogen into a dewar flask slowly, and again pouring the solvent into it, and then stirring the mixture continuously until the desired bath temperature is obtained. In

order to maintain a constant temperature, it is recommended that the mixture be kept slushy by occasionally blending, and by adding more liquid nitrogen when necessary. The bath temperatures were monitored by a type T thermocouple during an experiment. The baths consist of the following which was mixed with the liquid nitrogen: iso-pentane (113K), n-pentane (142K), ethanol (157K), isopropyl alcohol (184K).

3. Results and Discussion

3.1. Adsorption Isotherms

The adsorption isotherms for the Spherocharb and Sucrose Char are presented at various temperatures

from 77K to 184K. The x and y axes indicate the equilibrium pressure(atm) and amount adsorbed per sample weight(scc/mg) respectively. Fig. 3-7 show that the amount of nitrogen adsorbed on Spherocharb is larger than on Sucrose Char at the same temperature. It is found that the amount of nitrogen adsorbed on Spherocharb at 77K at a pressure of 0.52 atm is approximately 0.31scc/mg, while that on Sucrose Char at the same pressure is approximately 0.16scc/mg. It is also observed at 113K that the amount of nitrogen adsorbed on Spherocharb at the pressure of 0.86atm is approximately 0.24scc/mg, while that on Sucrose Char at the same pressure is approximately 0.15 scc/mg. In Fig. 8, and 10, the amount of nitrogen gas adsorbed

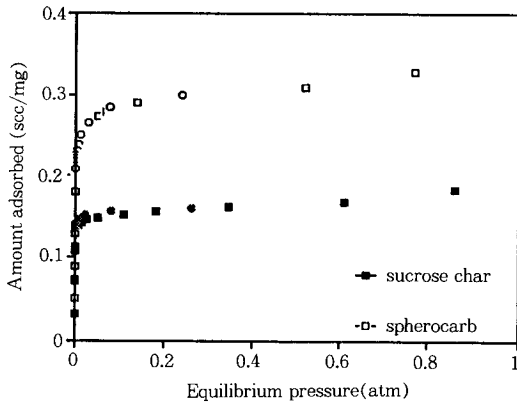


Fig. 3. Nitrogen adsorption at 77K : circle symbols indicates desorption.

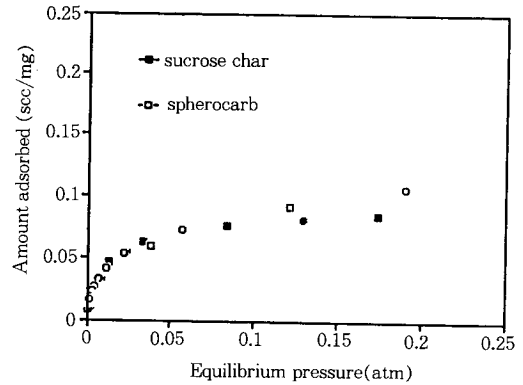


Fig. 5. Nitrogen adsorption at 142K : circle symbols indicates desorption.

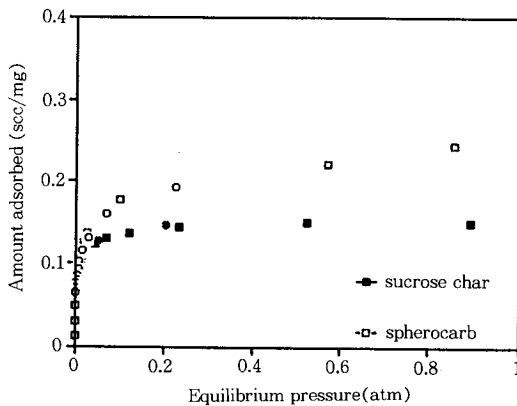


Fig. 4. Nitrogen adsorption at 113K : circle symbols indicates desorption.

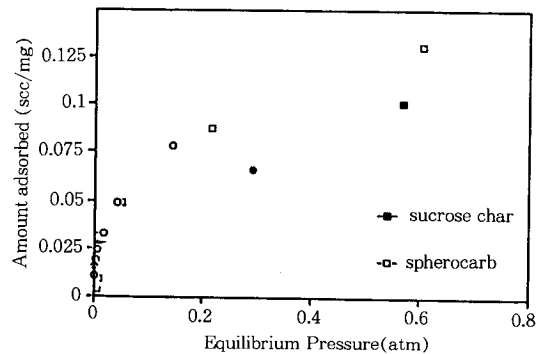


Fig. 6. Nitrogen adsorption at 157K : circle symbols indicates desorption.

by Spherocharb is shown to decrease with increasing temperature. Also, Fig. 9, and 11 show that the amount of nitrogen gas adsorbed by Sucrose Char decreases as the temperature of the isotherm is increased. It is observed that gases are strongly adsorbed at low pressures by both carbons. In the low relative pressure range of P/P_0 (up to 0.015), the amount of nitrogen gas by Spherocharb is approximately 0.25scc/mg. Here P_0 indicates the saturation vapor pressure, which is 1atm at 77K. This amount is almost 76 percent of the total amount of uptake at 77K. Also, in the low relative pressure range of P/P_0 (up to 0.016), the amount of nitrogen gas adsorbed by Sucrose Char is 0.14scc/mg,

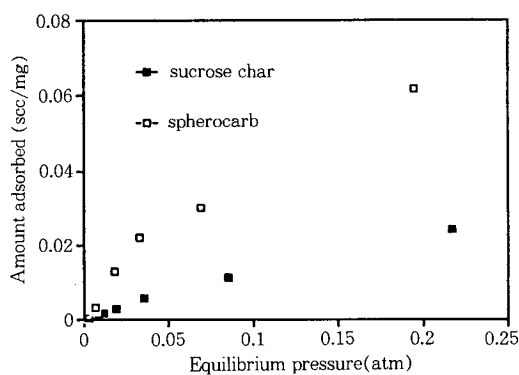


Fig. 7. Nitrogen adsorption at 184K : circle symbols indicates desorption.

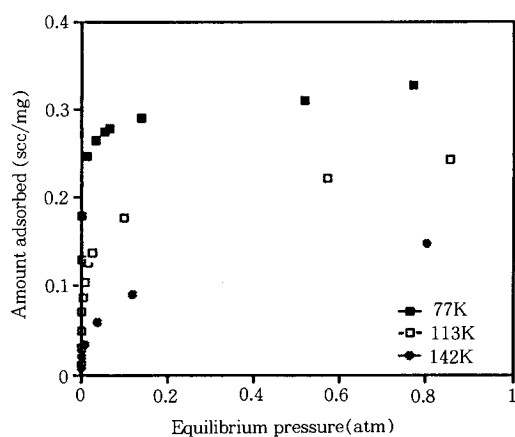


Fig. 8. Adsorption of nitrogen at 77K, 113K, and 142K on Spherocharb.

which is 79 percent of the total amount of uptake at 77K.

3.2. Brunauer Emmett Teller (BET) Model

The Brunauer–Emmett–Teller (BET) equation has become the most widely used standard equation for analyzing adsorption isotherms to determine specific surface areas of solids. The resulting equation for the BET equilibrium isotherm is as follows:

$$x/V(1-x) = 1/Vmc + (c-1)x/Vmc \quad (1)$$

where V is the amount adsorbed at P (equilibrium pressure), V_m is the monolayer coverage at P_0 (sat-

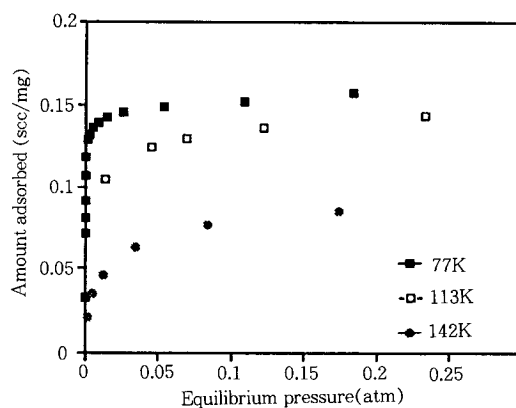


Fig. 9. Adsorption of nitrogen at 77K, 113K, and 142K on Sucrose Char.

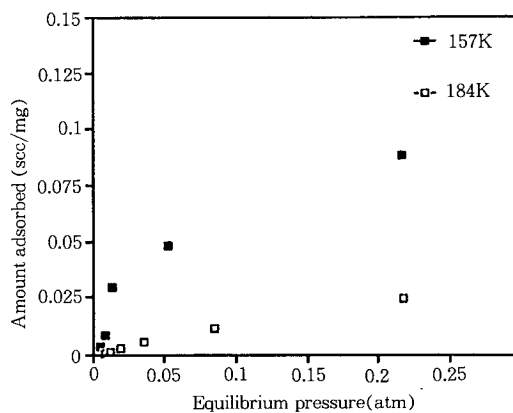


Fig. 10. Adsorption of nitrogen at 157K and 184K on Spherocharb.

uration vapor pressure), x is the equilibrium pressure of gas divided by saturation pressure of gas at 77K, P/P_0 , and c is expressed as follows:

$$\text{Exp}\{(q_1 - q_c)/RT\} \tag{2}$$

where q_1 is the heat of adsorption of the first layer, q_c is the heat of condensation, R is the gas constant, and T is the absolute temperature for adsorption. c is a dimensionless constant which is the characteristic value of the net heat of adsorption. However, the value of c can be used to characterize the shape of the isotherm in the BET plot, it does not provide a quantitative measure of the heat of adsorption.

The BET plots on Spherocharb and Sucrose Char at 77K (Fig. 12 and 13) show that linearity exists between $x=0$ and $x=0.1$. MacIver and Emmett[6] reported that the straight line of the BET plot for nitrogen on pure sodium chloride lies at a relative pressure up to 0.1. On rutile, Sing[7] obtained a linear BET plot for nitrogen over an appreciable range of P/P_0 (up to 0.2). In the original paper of Brunauer, Emmett, and Teller[8], BET plots are linear between relative pressures of about 0.05 and 0.35. Therefore, it is observed that although the BET equation requires a linear relation between $x/v(1-x)$ and x , the range of the straight line is, however, restricted to a limited part of the isotherm curve.

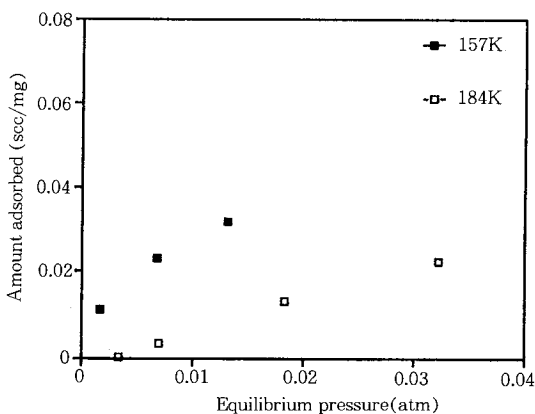


Fig. 11. Adsorption of nitrogen at 157K and 184K on Sucrose Char.

The model parameters, V_m and c , were obtained from the slope and intercept of the straight line. From the BET plot for nitrogen on Spherocharb at 77K (Fig. 12), the intercept, $1/(cV_m)$, was found to be 1.725×10^{-3} mg/scc and slope, $(c-1)/(cV_m)$, was found to be 3.842 mg/scc. Using these results, the values for V_m and c were calculated to be 260.14 cc/g and 2227 respectively. By the same manner, the parameter V_m and c in the BET equation for Nitrogen-Sucrose Char system at 77K were calculated to be 181.66 cc/g and 5639 respectively. The values of V_m will be used for the calculations of the specific areas of both carbons later.

3.3. Dubinin-Radushkevich Model

Dubinin and Radushkevich have proposed an em-

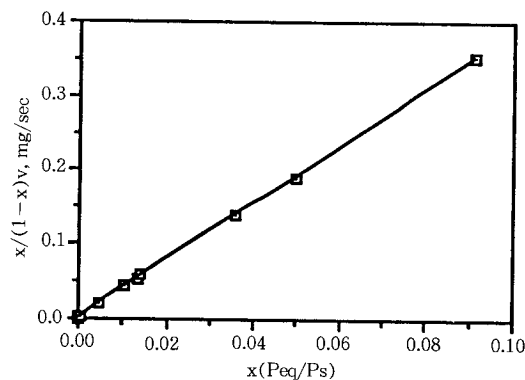


Fig. 12. BET plot for nitrogen on Spherocharb at 77K.

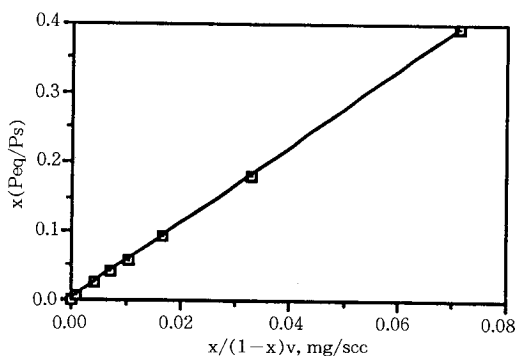


Fig. 13. BET plot for nitrogen on Sucrose Char at 77K.

pirical equation to describe the adsorption of gases on microporous solids. This equation has been extensively used in surface studies of carbons. The Dubinin-Radushkevich equation takes the form:

$$\log V = \log V_0 - (R^2 T^2) / (2.303 \beta E_0^2) \log^2 (P/P_0) \quad (3)$$

Where V_0 is the total micropore volume. V is the volume of adsorbate in porosity at relative pressure, P/P_0 , R is the gas constant, T is the absolute temperature, E_0 is the characterization energy parameter, and β is the adsorbate affinity coefficient. The characterization energy parameter is a function of the microporous structure of the adsorbent, and the adsorbate affinity coefficient describes the adsorbability that depends only on the adsorbate and is assigned unity for benzene which was chosen as an

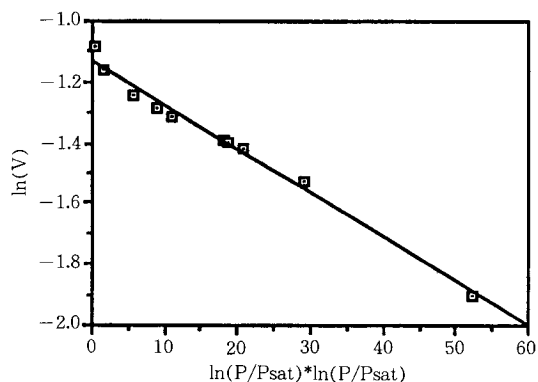


Fig. 14. DR plot of nitrogen on Spherochar at 77K.

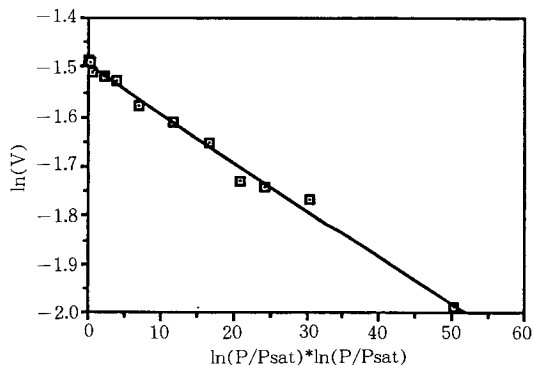


Fig. 15. DR plot of nitrogen on Sucrose Char at 77K.

arbitrary reference adsorbate by Dubinin. The adsorbate affinity coefficient for other vapors is relative to the affinity of benzene. Usually is assigned 0.33 for nitrogen.

Introducing a characteristic constant, D , the Dubinin-Radushkevich equation can be expressed as

$$\log V = \log V_0 - D \log^2 (P/P_0) \quad (4)$$

where D is equal to $(R^2 T^2) / (2.303 \beta E_0^2)$. According to this equation, the plot of $\log V$ against $\log^2(P/P_0)$ should be a straight line. The model parameters, $\log V_0$ and D , were obtained from the intercept and slope of straight line respectively. From the Dubinin-Radushkevich plot for nitrogen on the Spherochar at 77K (Fig. 14), the intercept was found to be -1.1285 and slope was found to be 0.0186 . The value of V_0 was calculated to be 0.324 cc/mg . In case of the Nitrogen-Sucrose system at 77K, the data fitting to the equation was made as shown in Fig. 15. By the same manner, the value of V_0 was obtained to be 0.224 cc/mg .

3. 4. Specific Surface Area and Micropore Volume

The specific surface area of graphites and porous carbons is usually determined from gas adsorption measurements using the Brunauer-Emmett-Teller (BET) theory. The Brunauer-Emmett-Teller equation has been accepted as the standard equation for analyzing adsorption isotherms to obtain specific surface areas of porous and non-porous solids. Nitrogen is recommended as an adsorptive in ASTM (C819)-77. To calculate the specific surface area it is necessary to obtain the value of V_m from the BET plot at first. Then, the specific surface area, S , of microporous carbons is calculated as:

$$S = (V_m a_m N_m P) / (RT) \quad (5)$$

Where V_m is the monolayer capacity, a_m is the specific surface area of nitrogen molecule at 77K, N_m is the Avogadro constant, R is the gas constant, and T is the absolute temperature. Although the choice of a value for a_m has been argued, Gregg

and Sing[9] recommended that the value a_m for nitrogen is 0.162 nm^2 .

The specific surface area of Spherocharb was obtained to be $1049 \text{ m}^2/\text{g}$, and that of Sucrose Char was obtained to be $733 \text{ m}^2/\text{g}$ by substituting the values of V_m into the above equation. From the results, it is found that the specific surface area of Spherocharb is about 43% larger than that of Sucrose Char.

Another method to calculate the surface areas of graphites and porous carbons is the Dubinin-Radushkevich approach. By substitution of V_o (micropore volume) values for Spherocharb and Sucrose Char into the above equation, the surface area of Spherocharb was calculated to be $1398 \text{ m}^2/\text{g}$ and that of Sucrose Char was calculated to be $900 \text{ m}^2/\text{g}$ respectively. Using these results, it is derived that the specific surface area of Spherocharb is about 55% larger than that of Sucrose Char.

Table 2 shows the comparison of specific surface areas of various carbons by Brunauer-Emmett-Teller method[4]. The specific surface area of Sucrose Char is about 8.5 times larger than that of Spheron 6 and 3.1 times larger than that of carbon black. Also, the specific surface area of Spherocharb is about 18.8 times larger than that of graphitized carbon black CT and 10.3 times larger than that of Vulcan 36-2700. It is figured that the JF005 carbon and carbon CA which were characterized by Rob-

erts et al[10]. And Rodriguez-Reinoso [11] have much higher surface area than carbon blacks or graphites, while they have similar specific surface areas as Spherocharb and Sucrose Char do. From these results, it is clearly reported that microporous carbons have much higher specific surface areas than carbon blacks or graphites.

From the experimental volume of nitrogen adsorbed at the relative pressure of 1, which is expressed as V_m , the total volumes of Spherocharb and Sucrose Char were determined by multiplying 1.55×10^{-3} , for cc. at S. T. P. to cc. of liquid nitrogen as recommended by Barrett et al[12]. This calculation was done based on the following assumptions:

1. Liquid nitrogen is packed inside micropores.
2. The density of the packed liquid nitrogen is $0.289 \text{ mol}/\text{cm}^3$.

The micropore volume of Sucrose Char was obtained to be $0.282 \text{ cm}^3/\text{g}$ and that of Spherocharb was obtained to be $0.403 \text{ cm}^3/\text{g}$. From these results, it is reported that the micropore volume of Spherocharb is about 40% larger than that of Sucrose Char.

4. Conclusions

It is accepted that for microporous carbons a value of surface area does not provide a unique property of the material. However, the comparison is necessary to characterize different carbons, although absolute numbers are not always significant. From this point of view, it is likely believed that the specific surface area is a relative parameter and not an absolute parameter. Therefore, it is concluded that the specific surface area of Spherocharb is about 1.5 times larger than that of Sucrose Char from the Brunauer-Emmett-Teller and Dubinin-Radushkevich method. Both carbons have much higher surface areas than carbon blacks or graphites. It is also concluded that the micropore volume of Spherocharb is about 1.4 times larger than that of Sucrose Char.

Table 2. Comparison of Specific Surface Areas of Various Carbons by BET Method

Carbon	Area(m^2/g)	Reference
Spheron 6	124	Gregg and Sing
Sterling FT-2700	11	Brown and Hall
Graphitized carbon black CT	39	Dubinin et al.
Vulcan 36-2700	71	Gregg and Sing
JF005*	882	Roberts et al.
Carbon CA*	1257	Rodriguez-Reinoso
Carbon black	337	Freeman and Kolb
Spherocharb*	733	Kim et al.
Sucrose Char*	1049	Kim et al.

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