

## 6Å MOLECULAR SIEVE PROPERTIES OF SARAN-TYPE CARBONS

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**Abstract**—The results of a molecular probe study on two Saran carbons prepared up to 1000°C and on polyvinylidene chloride carbons prepared up to 1500°C are reported. The Saran carbons adsorb appreciably more isobutane than neopentane over the whole carbonization range, indicating 6Å molecular sieve properties. Benzene and cyclohexane are also adsorbed to an appreciably greater extent than neopentane. Polyvinylidene chloride carbons prepared at comparable temperatures adsorb neopentane freely; neopentane molecular sieve effects are only observed for samples heated above 1200°C. It is concluded that the observed molecular sieve effects are due to slit-shaped pore constrictions having a size between ca. 4.5 and 5.7Å in thickness and connecting cavities of at least ca. 12Å in thickness.

### 1. INTRODUCTION

THE adsorptive properties of Saran† carbons were first investigated in detail by PIERCE, *et al.*<sup>(1)</sup> This has been followed by additional adsorption studies on Saran carbons<sup>(2,3)</sup> and on carbons derived from pure polyvinylidene chloride (PVDC)<sup>(4-10)</sup> and polyvinyl chloride (PVC).<sup>(7,8)</sup> X-ray diffraction studies have also been made on carbons produced from these polymers.<sup>(11,12)</sup> PVDC carbon is open structured, highly cross-linked, and non-graphitizing; PVC carbon is compact and graphitizing.<sup>(11)</sup>

There has been considerable interest in the molecular sieve properties of PVDC carbons heated to maximum temperatures between 700-800°C. These carbons have been found to have a negligible capacity for  $\alpha$ -pinene (minimum cross-section of ca. 8Å) and a significant capacity for neopentane (minimum cross-section of ca. 6.2Å).<sup>(5,7)</sup> These carbons are hard and strong. In contrast, PVC carbons prepared at 700°C have pores primarily less than ca. 6Å in diameter, show a negligible capacity for neopentane, and have a

smaller total pore volume than do PVDC carbons.<sup>(7,8)</sup> Further, PVC carbon is relatively soft and weak; its use as a molecular sieve carbon in fixed or fluid operations appears limited.

The possibility of producing PVDC based carbons with the majority of the pores around 6Å (so as to exclude neopentane) has been investigated in this study. Two approaches have been followed. In the first, PVDC carbons have been heated at temperatures above 1000°C, at which temperatures sintering occurs and the average pore size decreases.<sup>(13)</sup> In the second approach, medium-temperature Saran carbons have been produced. It was felt the possibility that the carbon derived from the vinyl chloride portion of the copolymer, Saran, would have the desired "tailoring effect" on the basic PVDC pore structure (that is, decrease its pore size) should be examined. The possibility of "tailoring effects" in this system has been discussed recently.<sup>(14)</sup>

### 2. EXPERIMENTAL

Polyvinylidene chloride was prepared as described in detail by MARSH and WYNNE-JONES.<sup>(9)</sup> Samples of Saran were obtained from the Dow Chemical Company. The ratio of the vinylidene chloride to vinyl chloride in both Saran 428 and Saran 489 was given as 90:10. In addition, Saran 428 also contained about 2% plasticizer. The Saran

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†Copolymer consisting of 80-90% polyvinylidene chloride and various amounts of polyvinyl chloride and plasticizer.

TABLE 1. COMPOUNDS USED IN MOLECULAR PROBE STUDIES

Compounds	Adsorption Temp., °C	Minimum Cross-section, Å	Molecular Area, Å <sup>2</sup>
Carbon dioxide	-77	3.3 <sup>(28)</sup>	17 <sup>(22)</sup>
Butane	0	4.3 <sup>(26)</sup>	47 <sup>(21)</sup>
Isobutane	0	5.0 <sup>(28)</sup>	51 <sup>(21)</sup>
Neopentane	0	6.2 <sup>(28)</sup>	62 <sup>(21)</sup>
Benzene	40	3.7, 7.0 <sup>(7)</sup>	—
Cyclohexane	40	4.8, 6.8 <sup>(7)</sup>	—

samples were supplied in a -100 mesh and were used as such. The PVDC carbon was ground after carbonization to -100 mesh. A heating rate of 7.5°C/min was used up to 1000°C; and 15-30°C/min, from 1000 to 1500°C. A carbonization soak time of 4 hr was used for all samples.

The extent of uptake of the adsorbates listed in Table 1, at a relative pressure of 0.5, was measured gravimetrically, using quartz helical springs. The extent of adsorption was measured after 1 hr; and, thus, the adsorptive capacities are not necessarily equilibrium values.

### 3. RESULTS AND DISCUSSION

There has been extensive deliberation on the correctness of calculating surface areas from the Type I isotherm, encountered for adsorption on microporous carbons, in terms of the Langmuir<sup>(15)</sup> or modified BET equation.<sup>(16)</sup> Many authors

consider that the adsorption process is one of reversible capillary filling of the micropores, rather than adsorption being restricted to monolayer formation.<sup>(17-20)</sup> Nevertheless, Lamond and Marsh have argued that the surface area values for unactivated carbons are sensibly correct.<sup>(19)</sup> Perhaps the notation of BARRER,<sup>(20)</sup> where the adsorptive capacity is measured at a point on the flat portion of the isotherm and is expressed in terms of "monolayer area equivalent", is most suitable. Our adsorption results have been calculated in such fashion and are depicted in Figs. 1-3.

The very high surface areas (1000 m<sup>2</sup>/gm) for Saran carbons prepared above 500°C and the significant separation between isobutane and neopentane adsorption for Saran 489 carbons prepared above 800°C and for Saran 428 carbons prepared over the whole temperature range examined are

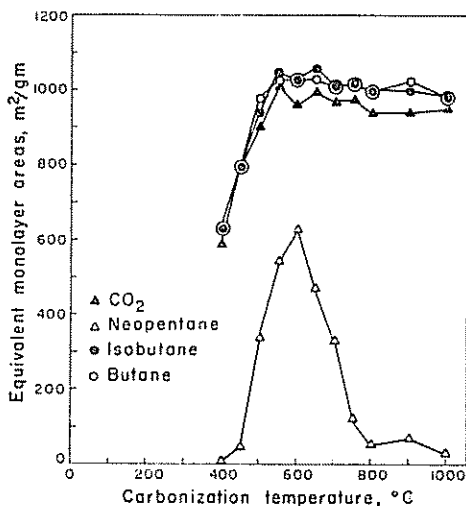


FIG. 1. Surface Areas of Saran 489 Carbons.

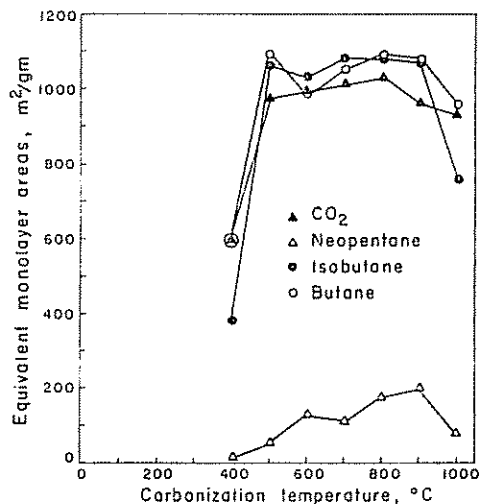


FIG. 2. Surface Areas of Saran 428 Carbons.

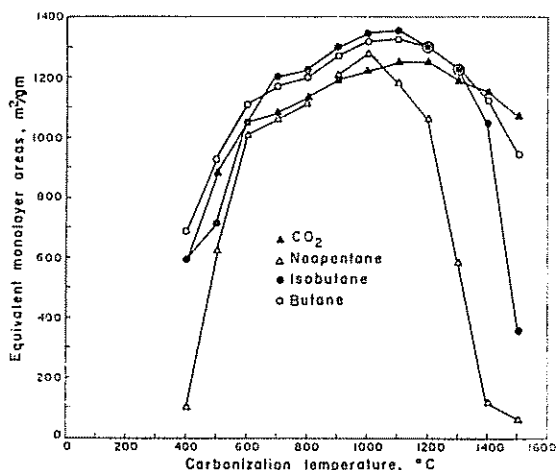


FIG. 3. Surface Areas of Polyvinylidene Carbons.

noteworthy. The observed, sharp maximum in the neopentane adsorption at 600°C (630 m<sup>2</sup>/gm) for the Saran 489 carbon contrasts sharply with the low adsorption for the Saran 428 carbon over the entire carbonization range. The difference in the polymers is that the latter contains 2% plasticizer, whose carbonization products must be influencing the pore structure of the resultant carbon.

The areas for the PVDC carbon (Fig. 3) go through a maximum of ca. 1300 m<sup>2</sup>/gm for a carbonization temperature of 1000°C—a maximum

area significantly higher than that found for the Saran carbons. As evident by the large neopentane areas of the PVDC carbons prepared up to 1200°C, their pore size is somewhat larger than that of Saran carbons prepared at equivalent temperatures. MARSH and WYNNE-JONES<sup>(9)</sup> and DUBININ<sup>(13)</sup> have reported on the high thermal stability of PVDC carbons. In the present work, it is apparent that the majority of the pores only shrink to below 6Å in the temperature range 1200–1400°C.

The variation of pore volume, accessible to the various probes, with heat treatment temperature is depicted in Fig. 4. Values included for the 700°C Saran 428 carbon are very similar to the 1400°C PVDC carbon.

The close agreement between the butane, isobutane and neopentane areas for PVDC carbons up to 1200°C (Fig. 3) indicates that the molecular area values of WYNNE-JONES<sup>(21)</sup> (Table 1), calculated by comparison with nitrogen as a standard (16.2Å<sup>2</sup>), are consistent. The carbon dioxide areas (based upon 17.2Å<sup>2</sup>)<sup>(22)</sup> are approximately 8% lower than the hydrocarbon areas; taking a value of 20.5Å<sup>2</sup><sup>(2,23)</sup> as the molecular area would overcorrect by ca. 8%.

The pore size of zeolite molecular sieves can be determined accurately by X-ray analysis.<sup>(24)</sup> Correlation of the adsorption data on these materials has shown that molecules have an appreciable activation energy for diffusion when the pore

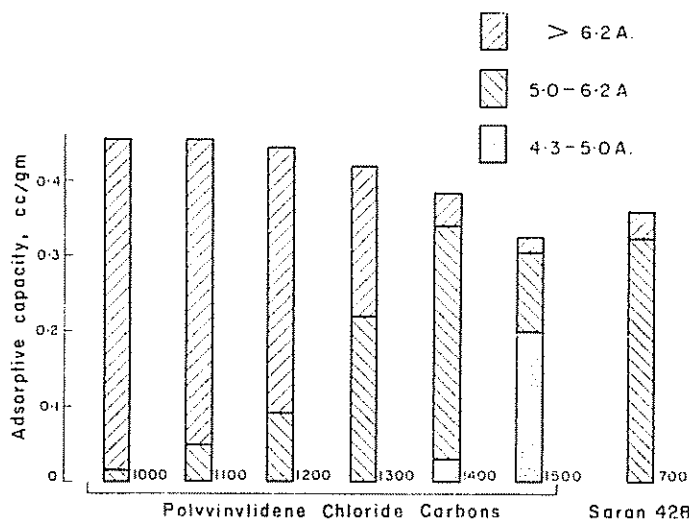


FIG. 4. Histogram of Adsorptive Capacities of Various Carbons.

is about 0.5Å smaller than the minimum collision diameter of the molecule.<sup>(25)</sup> By analogy, we can say that a negligible number of pores and/or pore constrictions greater than ca. 5.5 to 6.0Å are present in the carbons when low neopentane areas are observed.

WOLFF<sup>(26)</sup> has suggested, although probably not on conclusive evidence, that the pores of activated carbons are slit shaped. WALKER *et al.*,<sup>(27)</sup> found higher adsorption for benzene and cyclohexane than for neopentane on a series of 5Å Composite Carbon Molecular Sieves (made by coating granular activated carbon particles with a thermosetting polymer, followed by curing and carbonization of the polymer layer) which clearly indicated the slit-like nature of the pores. The authors, however, were unable to determine whether the slit-like nature of the pores resulted from the geometry of the activated carbon substrate or was purely an effect of the polymer coating. Similar comparisons of benzene and cyclohexane adsorption have been made on the Saran 428 carbons (Table 2). Both benzene and cyclohexane are adsorbed to a greater extent than neopentane, suggesting a structure of slit-like pores and/or pore constrictions of less than ca. 5.7Å in thickness and greater than ca. 7.0Å in width. The fact that isobutane adsorption is substantial for the Saran 428 carbons heated between 500–900°C indicates that the thickness of most of the pores is greater than ca. 4.5Å.

It is difficult to think of the molecular sieve effects in terms of uniform pores. The equivalence of the carbon dioxide, butane, isobutane and neopentane areas up to 1000°C heat treatment for the PVDC carbons suggests that the majority of the

void volume is situated in pores of at least two neopentane diameters. On sintering at 1400°C, the neopentane area drops to less than 10% of its maximum value, while the isobutane area decreases only slightly. Shrinkage of a uniform pore structure to a point where it still admits at least two layers of isobutane should result in its admitting at least one layer of neopentane. Thus, sintering at 1400°C would be expected to have only decreased the neopentane area to ca. 50% of its maximum value or to 640 m<sup>2</sup>/gm. The very low neopentane area for PVDC carbon after heat treatment to 1400°C suggests the existence of a pore system containing cavities connected by pore constrictions, with most of the surface area and pore volume in the cavities. For PVDC heated to 1000°C, the pore system consisted of cavities greater than two neopentane diameters (ca. 12Å) in size and constrictions only slightly larger than ca. 5.7Å in thickness. Heating to 1400°C resulted in shrinking the pore constrictions below 5.7Å (making the cavities inaccessible to neopentane). Some shrinkage of the cavities will also occur, but they remained at least greater than two isobutane diameters in thickness.

Using a similar argument, it is concluded that the Saran 489 carbons also have a pore system consisting of cavities connected by constrictions. That is, upon heating this carbon from 600 to 800°C, the neopentane area decreased from 630 to 50 m<sup>2</sup>/gm, while the isobutane area underwent a negligible decrease.

The observed separation ratios for the Saran carbons and the 1400°C PVDC carbon are of the order of from 10–20 to 1—similar to the ratios observed (but for different adsorbates) for the zeolite molecular sieves.<sup>(25)</sup> The latter have a

TABLE 2. ADSORPTIVE CAPACITIES OF SARAN 428 CARBONS

Carbonization Temp., °C	Adsorbate Uptake, cc of liquid/gm				
	Butane	isobutane	neopentane	Benzene	Cyclohexane
400	0.202	0.120	0.0034	—	—
500	0.373	0.329	0.0173	0.353	0.301
600	0.332	0.332	0.0445	0.341	0.317
700	0.360	0.360	0.0360	0.350	0.325
800	0.373	0.370	0.0595	0.337	0.326
900	0.369	0.360	0.0680	—	—
1000	0.302	0.238	0.0204	—	—

regular crystalline structure, with spherical cavities of the order of 12Å in diameter, which are accessible through windows of 3.5, 4.2, 8.0 and 9.0Å in diameter. Amorphous carbons do not have a regular crystalline structure. However, results of this study show that carbons can be made which have a system of cavities connected by slit-shaped pore constrictions less than ca. 6Å in thickness and adsorption capacities comparable to those of the zeolites. At the moment, there is no commercial zeolite available with an aperture size of ca. 6Å. Therefore, possible uses for Saran and PVDC carbons appear promising.

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#### REFERENCES

1. PIERCE C., WILEY J. W. and SMITH R. N., *J. Phys. Chem.* **53**, 669 (1949).
2. CULVER R. V. and HEATH N. S., *Trans. Faraday Soc.* **51**, 1569 (1955).
3. HEATH N. S. and CULVER R. V., *Trans. Faraday Soc.* **51**, 1575 (1955).
4. EVERETT D. H., REDMAN E., MILES A. J. and DAVIES D. H., *Fuel* **11**, 219 (1963).
5. DACEY J. R. and THOMAS D. G., *Trans. Faraday Soc.* **50**, 647 (1954).
6. DACEY J. R., CLUNIE J. C. and THOMAS D. G., *Trans. Faraday Soc.* **54**, 250 (1958).
7. KIPLING J. J. and WILSON R. B., *Trans. Faraday Soc.* **56**, 557 (1960).
8. KIPLING J. J. and WILSON R. B., *Trans. Faraday Soc.* **56**, 562 (1960).
9. MARSH H. and WYNNE-JONES W. F. K., *Carbon* **1**, 269 (1964).
10. LAMOND T. G. and MARSH H., *Carbon* **1**, 293 (1964).
11. FRANKLIN R. E., *Proc. Roy. Soc.* **209A**, 196 (1951).
12. WINSLOW F. H., BAKER W. O. and YAGER W. A., *Proc. of the First and Second Carbon Conference*, p. 93. Univ. of Buffalo (1956).
13. DUBININ M. M., *Proc. of the Fifth Carbon Conference*, Vol. 1, p. 81, Pergamon Press, New York (1962).
14. TAGER A. A., TSILIPOTKINA M. V., ROMANOVA P. M. and DUBININ M. M., *Dokl. Akad. Nauk., SSSR* **144**, 602 (1962).
15. LANGMUIR I., *J. Am. Chem. Soc.* **40**, 1361 (1918).
16. JOYNER L. B., WEINBERGER E. B. and MONTGOMERY C., *J. Am. Chem. Soc.* **67**, 2182 (1945).
17. GREGG S. J. and STOCK R., *Trans. Faraday Soc.* **53**, 1355 (1957).
18. DUBININ M. M., *Industrial Carbon and Graphite*, Soc. of Chemical Industry, London, p. 219 (1958).
19. LAMOND T. G. and MARSH H., *Carbon* **1**, 281 (1964).
20. BARRER R. M., *Proc. of the Tenth Symposium of the Colston Research Society*, p. 50. Butterworths, London (1958).
21. WYNNE-JONES W. F. K., *ibid*, p. 35.
22. EMMETT P. H., *Symposium on New Methods for Particle Size Determination in the Subsize Range*, p. 97. Am. Soc. for Testing Materials, Philadelphia (1941).
23. KIPLING J. J., SHERWOOD J. N., SHOOTER P. V. and THOMPSON N. R., *Carbon* **1**, 321 (1964).
24. REED T. B. and BRECK D. W., *J. Am. Chem. Soc.* **78**, 5972 (1956).
25. BRECK D. W., EVERSOLE W. G., MILTON R. M., REED, T. B. and THOMAS T. L., *J. Am. Chem. Soc.* **78**, 5963 (1956).
26. WOLFF W. F., *J. Phys. Chem.* **62**, 829 (1958).
27. WALKER P. L. Jr., LAMOND T. G. and METCALFE J. E., III, *Preprint to Industrial Carbon and Graphite Conference*, London (1965).
28. BRECK D. W., Private Communication (1963).