

Determination of Micropore Volumes of Active Carbons Using Nonane Preadsorption and Isotherm Subtraction

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ABSTRACT

Micropore volumes, V_0 , and residual surface areas, S' , for an activated series of carbons were estimated by application of the isotherm subtraction (IS) and nonane pre-adsorption (NP) methods to N_2 isotherms. For carbons with narrow micropores V_0 and S' values obtained by the NP and IS methods were in good agreement. For carbons with wide micropores the NP method substantially underestimated V_0 and overestimated S' since nonane was not retained in wide micropores. For such carbons application of the IS method to the NP residual isotherm removed the microporous contribution to adsorption and gave V_0 and S' values in good agreement with those obtained by the IS method.

INTRODUCTION

Although active carbons are essentially microporous, there is usually a continuous distribution of pore sizes extending into the mesopore size range. It is useful to be able to estimate the microporous and non-microporous contributions to adsorption, for example, as a micropore volume, V_0 , and a residual (non-microporous) surface area, S' , which includes the surface areas of mesopores, macropores and external surface. Nonane pre-adsorption (NP) has been shown to be effective in determining V_0 and S' for moderately activated carbons (1), but, for highly activated carbons V_0 is under-estimated and S' is over-estimated because nonane is not retained in some wide micropores. Isotherm subtraction (2) or decomposition (3) is a simple method for estimating S' using a single adsorption isotherm. In a recent study (2) the IS and NP methods were compared for adsorption of Ar at 77K on anthracite-based active carbons. It was shown that the two methods give comparable results, small discrepancies being attributable to the deficiencies of the NP method when applied to carbons with wide micropores. In this paper the comparison of the two methods is extended by application to a different adsorbent-adsorptive system, which has been the subject of intensive study (1,4).

EXPERIMENTAL

A series of active carbons with a wide range of burn-off was prepared by reaction of an active carbon, obtained from olive stones, with dry air at 623K; details of the methods

used have been described (4). Adsorption of N_2 at 77K was carried out gravimetrically using conventional spring balances. Details of the adsorption and nonane pre-adsorption methods have also been described (1,4).

RESULTS AND DISCUSSION

Some examples of total isotherms and residual isotherms obtained by the NP and IS methods are in Fig. 1. For all of the carbons the residual isotherm obtained after nonane pre-adsorption is greater than the IS residual isotherm. BET surface areas and constants, C , for the total and residual isotherms are in Table 1; carbon number, eg. B-6, denotes a carbon gasified to 6% burn-off. The total surface areas must be regarded as nominal since they include a microporous contribution. However, qualitative changes in the pore structure of the carbons, as a result of gasification, may be inferred from changes in S and C . In the initial stages of gasification (carbons B-6 and B-10) there is evidence for development of open, fine microporosity since S and C increase. Subsequently, surface areas increase to a maximum at about 20 to 31% burn-off and then decrease, while the decreasing values of C , for carbons B-20 to B-52, are evidence for a progressive increase in mean pore size as a result of gasification. The increase in C for carbon B-71 indicates that some new, open microporosity is created in the later stages of gasification.

Micropore volumes, V_0 , (Table 2) were estimated by extrapolation of the linear,

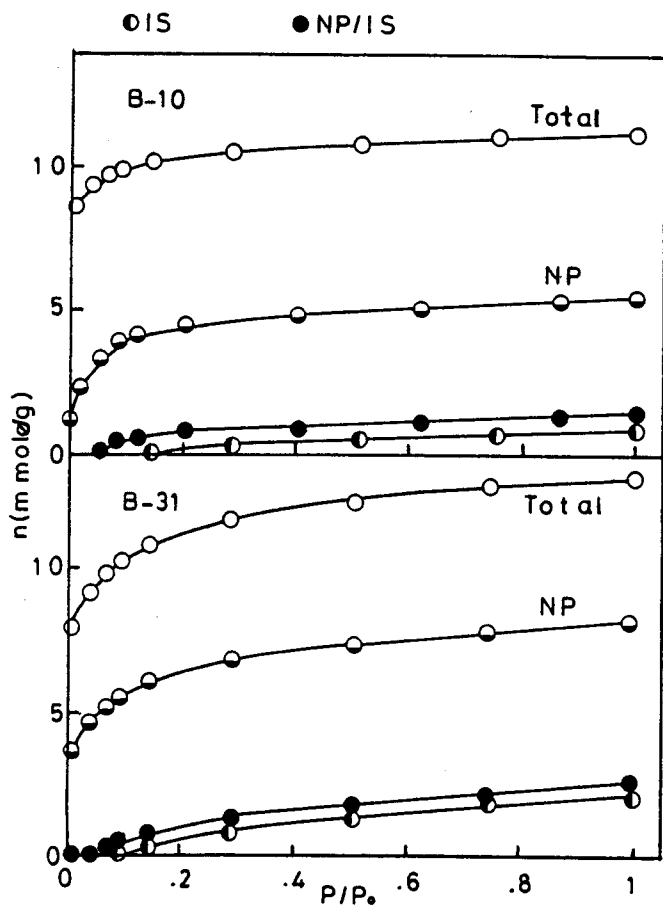


Figure 1.-Adsorption isotherms of N_2 at 77K

Table 1: BET surface areas (m^2/g) and BET "C" constants.

Carbon number	Total isotherms		Residual isotherms		
	S	C	IS method	NP method	Corrected NP method
B- 6	838	1780	19	88	—
B-10	881	2210	25	72	—
B-20	932	850	117	241	103
B-31	923	750	92	379	134
B-42	718	450	129	368	132
B-52	640	400	142	226	96
B-71	455	490	50	102	—

Cross sectional area of N_2 at 77K = 0.162 nm^2 .

low pressure part of the Dubinin-Radushkevich (DR) isotherm and from the vertical separation at $P/P_0 = 0.8$ of the total isotherms and the residual isotherms obtained by the NP and IS methods. As expected, for all carbons V_0 values from the DR equations and the IS method are in good agreement. For carbons B-6, B-10 and B-71, V_0 obtained by the NP method is in agreement with values obtained by the other two methods (to within $\pm 0.02 \text{ ml/g}$). For the other carbons, the NP methods appears

Table 2: Micropore volumes (ml/g)

Carbon number	DR method	IS method	NP method	Corrected NP method
B- 6	.35	.34	.33	—
B-10	.37	.36	.35	—
B-20	.38	.37	.29	.38
B-31	.40	.38	.23	.38
B-42	.30	.29	.18	.30
B-52	.26	.25	.19	.26
B-71	.19	.18	.18	—

N_2 liquid density at 77K = 0.808 g/ml .

to under estimate substantially the micropore volume. These discrepancies are because nonane is not retained in the wide micropores which have been developed in these carbons by gasification. The same findings were reached in an earlier study of these carbons (1) and Ali and McEnaney reached similar conclusions for adsorption of Ar on anthracite-based carbons (2).

The limitations of the NP method when applied to carbons containing wide micropores are also revealed by the BET analyses of the residual isotherms, Table 1. For carbons B-20 to B-52 the residual surface areas and C values obtained by the NP method ($C=106$ to 158) are substantially larger than those obtained by the IS method ($C=2$ to 5), indicating that there are significant microporous contributions to the NP residual isotherms. Attempts were therefore made to remove the microporous contributions by application of the isotherm subtraction method to the NP residual isotherms for carbons B-20 to B-52. Examples of the NP and IS residual isotherms and the corrected NP residual isotherms (denoted as NP/IS) are compared in Fig. 1. In each case the corrected NP residual isotherm is nearly coincident with the IS residual isotherm. The corrected NP micropore volumes (Table 2) agree with those obtained by the DR and IS methods applied to the total isotherms. The corrected residual surface areas also agree with those obtained by the IS method withing experimental uncertainty, since $\pm 0.02 \text{ ml (liquid } N_2)/g$ is equivalent to $\pm 56 \text{ m}^2/g$.

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