

THERMAL TREATMENT OF NON-POROUS SILICA, LIMITED CHANGES IN THE MAGNITUDE OF THE BET-C CONSTANT AND THEIR INFLUENCE ON ADSORPTION: REFERENCE DATA FOR CARBON TETRACHLORIDE ADSORPTION

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ABSTRACT

Degussa Aerosil TK800 was thermally dehydrated in vacuo over the temperature range 20–900°C. Adsorption measurements were carried out using as adsorbates both nitrogen, at liquid-nitrogen temperature, and carbon tetrachloride vapor, at 35°C. On varying the extent of thermal dehydration, marked changes in the magnitude of the BET-C constant were produced; meanwhile various non-porous samples were also formed. The non-porous reference samples were used to construct some recently developed V/V_m , P/P_0 curves. The reference data for carbon tetrachloride adsorption is presented and discussed.

INTRODUCTION

As previously reported [1,2], different non-porous silica aerosils have been used concurrently to construct reference data for nitrogen adsorption. In recent work based on such non-porous reference materials, silica Aerosil TK800 has been used to construct some reference data for organic adsorbates, and it is used here to construct similar data for carbon tetrachloride. On comparing nitrogen adsorption isotherms [3] with those determined from carbon tetrachloride adsorption, some common samples appear to have no porosity characteristics, and may thus be viewed as *non-porous reference standards* for carbon tetrachloride adsorption.

The measurable changes in magnitude of the BET-C constant observed for various non-porous reference samples will be considered as a measure of the extent of surface/adsorbate interaction. If the adsorption isotherms of carbon tetrachloride do not show hysteresis effects (cf. those of nitrogen), the adsorption values, V/V_m , are essentially viewed as *reference adsorption data*.

Reference values, V/V_m , were frequently used to monitor other parameters of porosity, such as pore structure and the location of adsorbate molecules. Furthermore, the assessment of the specific surface area for other porous samples becomes possible. Different reference data are thus required to cover the measurable changes in the nature of surface/adsorbate interactions (BET-C) as well as the effects of using different vapor adsorbates such as water, methanol, cyclohexane, carbon tetrachloride, etc.

The lack of appropriate reference data for carbon tetrachloride adsorption was partially dealt with, and some recently constructed V/V_m , P/P_0 curves were introduced. In comparison with another report [4] where BET-C \approx 4–32, the present study extends over a relatively wider change in the magnitude of the BET-C constant, namely 4–62, and includes four n_R , P/P_0 curves, covering narrower ranges of the BET-C constant, namely, 4–6, 15–19, 36–37 and 61–62.

EXPERIMENTAL

Silica Aerosil TK800 was thermally dehydrated in vacuo for 4 h at a series of temperatures, namely 20, 110, 200, 290, 380, 480, 510 and 900°C, which were identical to those used by previous workers [3,5]. These samples were designated as $T(20)$, $T(110)$, $T(200)$, $T(290)$, $T(380)$, $T(480)$, $T(510)$ and $T(900)$, respectively.

Heating was carried out using a small electrical tubular furnace programmed to increase the temperature at a rate of 2.5–3.0°C min⁻¹.

Adsorption of nitrogen at liquid-nitrogen temperature [6], and adsorption of carbon tetrachloride at 35°C [7] were both carried out using conventional volumetric apparatus.

RESULTS AND DISCUSSION

Nitrogen-specific surface areas, S^{N_2} , were obtained by applying the BET-method to the nitrogen adsorption isotherms in the range 0.05–0.35 P/P_0 , and adopting the value 16.2 Å² for the cross-sectional area of the nitrogen molecule [8]. The adsorption data were discussed in a previous paper [3].

Surface areas of carbon tetrachloride, S^{CCl_4} , were also obtained by applying the BET-method to the adsorption isotherms in the range 0.05–0.25 P/P_0 and adopting the value of 30 Å² for the cross-sectional area of the carbon tetrachloride molecule [9,10], which may be regarded as a symmetrical sphere. The cross-sectional area is calculated using the equation of Emmett and Brunauer [9] and the molecular packing factor 1.091.

$$a = 1.091(M/\rho N)^{2/3} \times 10^{16}$$

where M is the molecular weight of adsorbate, N is Avogadro's number and ρ is the density of the bulk liquid.

The adsorption isotherms were invariably of type II using the classification of Emmett and Brunauer [9]. As I reported earlier [3], nitrogen adsorption isotherms appear to exhibit no detectable hysteresis effects at temperatures above 110°C; therefore, the isotherms of carbon tetrachloride adsorption were determined for samples dehydrated above 110°C, thus providing isotherms which show no hysteresis effects. It can be seen that the adsorption isotherms obtained exhibit high-pressure hysteresis loops which end at relative pressures 0.70–0.80 P/P_0 and only the sample $T(900)$ seems to have no hysteresis effects. Based on previous observations, the presence of this

high-pressure hysteresis indicates the occurrence of marked intergranular condensation (of the adsorbate) rather than detectable porosity characteristics.

The surface areas, S^{CCl_4} , BET-C constants and values of S_t ($\text{m}^2 \text{g}^{-1}$) are all listed in Table 1. S_t values were calculated by application of the V_1-t method [1,11] using earlier data [4] as *reference standards*. This seems to cover the changes in magnitude of the BET-C constant and to satisfy the criteria for correct analysis [1,11]. The agreement between the surface areas, S^{CCl_4} , and S_t ($\text{m}^2 \text{g}^{-1}$) is taken as a justification of the choice of the reference data [4] for the proposed analysis.

As pointed out by Brunauer [12], in the analysis of an isotherm by the t -method, it is essential that a correct t -curve is employed. It is suggested that the appropriate t -curve should be based not on the chemical similarity of the adsorbent surface, but rather on the magnitude of the heat of adsorption. According to Brunauer, the magnitude of BET-C is frequently considered to be an adequate measure for testing the appropriateness of the t -curve, but that the measure of agreement between S_{BET} and S_t is a more reliable check. Furthermore, Brunauer [12] has pointed out that the BET-C constant is directly related to the free energy of adsorption (or change in chemical potential) rather than to the heat of adsorption; thus the magnitude of the BET-C constant also depends on the P/P_0 range of linearity of the BET-plot.

Reference to the second column of Table 1, shows that the values of the BET-C constant for samples $T(290)$ and $T(480)$ appear to represent the limited BET-C range 15–19; also, for samples $T(380)$ and $T(510)$, a BET-C range of about 4–6 was introduced.

For samples $T(380)$ and $T(510)$, the BET-surface areas S^{CCl_4} are much bigger than S_t ($\text{m}^2 \text{g}^{-1}$), despite the apparent fulfilment of the criteria for a correct analysis. The marked disagreement between S^{CCl_4} and S_t ($\text{m}^2 \text{g}^{-1}$) shows that the reference data [4] are less applicable for low BET-C values.

This investigation deals with some limited changes in the free energy of adsorption (as related to the magnitude of BET-C) and their respective influence on n_R , P/P_0 curves.

The t -values are basically calculated by multiplying the statistical number

TABLE 1

Adsorption characteristics of carbon tetrachloride on TK800 samples

Sample	BET-C constant	S^{CCl_4} ($\text{m}^2 \text{g}^{-1}$)	S_t ($\text{m}^2 \text{g}^{-1}$)
$T(200)$	36–37	53.2	50
$T(290)$	18–19	28.5	30
$T(380)$	4–5	47.0	28
$T(480)$	15–16	32.8	35
$T(510)$	5–6	51.3	36
$T(900)$	61–62	23.8	—

of monolayers, n_R , by the unilayer thickness, t_m , further details being mentioned elsewhere [13,14].

$$n_R = V/V_m; \quad t = n_R t_m$$

The V/V_m vs. P/P_0 curves for some selected samples $T(200)$, $T(290)$, $T(380)$ and the reference data [4] for $BET-C \approx 4-32$ are graphically represented in Fig. 1. The increase in the BET-C constant was followed by a marked increase in reduced adsorption values, V/V_m , hence more gas adheres to the surface when the free energies of adsorption are higher.

Sample $T(380)$: $BET-C \approx 4-5$ shows markedly low adsorption values, V/V_m , starting from the lower pressures and continuing to the saturation pressure, $P/P_0 = 1.0$. As is evident, the occurrence of intergranular capillary condensation seems to be dominant above $P/P_0 = 0.85$.

Sample $T(200)$: $BET-C \approx 36-37$ gives a V/V_m vs. P/P_0 curve which agrees well with the reference data [4] for $BET-C \approx 4-32$ at low pressures and continues to $P/P_0 = 0.50$. At higher relative pressures ($P/P_0 > 0.50$), the reference data [4] assumes higher adsorption values, V/V_m , which continue to the saturation pressure. The measurable high adsorption values (V/V_m) of the reference data [4] at intermediate pressures indicates that the reference material contained some wide- and/or meso-pores, which naturally lead to marked multimolecular adsorption.

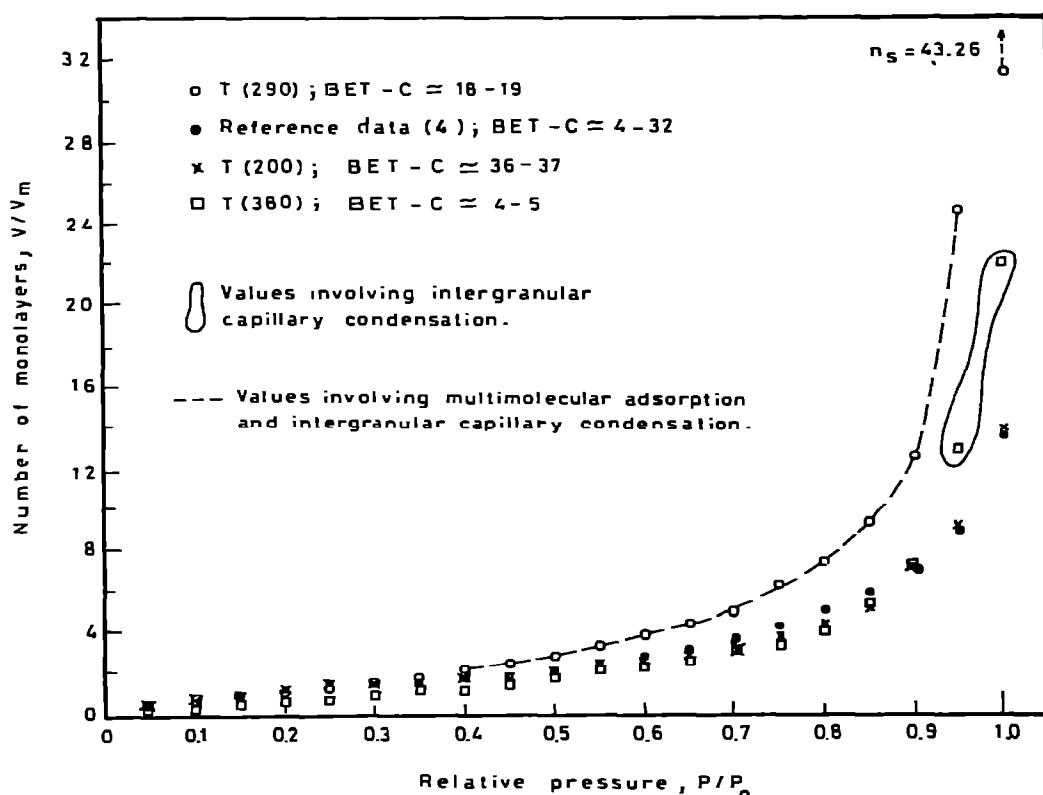


Fig. 1. V/V_m vs. P/P_0 curves for some TK800 samples.

For sample *T*(290): BET-C \approx 18–19, the high V/V_m values obtained at relative pressures $P/P_0 > 0.30$ are related to the limited porosity of the sample, as established from nitrogen adsorption measurements [3] and only the adsorption isotherm of sample *T*(290) exhibits a limited hysteresis loop which ends at $P/P_0 = 0.65$, indicating limited porosity in the sample investigated. The adsorption values (V/V_m) at low pressures ($P/P_0 < 0.30$) on adsorbents that *only* contain wide pores should be identical to the adsorption on a free non-porous adsorbent [13], so long as the magnitude of their BET-C constant is nearly identical. The enhanced V/V_m values at $P/P_0 > 0.30$ (cf. Fig. 1) indicates the occurrence of measurable multimolecular adsorption at intermediate pressures and then the latter intergranular capillary condensation continues to the saturation pressure, $P/P_0 = 1.0$.

The reference statistical V/V_m values for sample *T*(290) at relative pressures $P/P_0 > 0.30$ was basically reproduced from sample *T*(200). The aspects of using different adsorption isotherms which widely differ in their chemical nature to construct reference curves was reported earlier by Lippens et al. [1] and by Hagymassy et al. [14].

The different V/V_m values for these samples are listed in Table 2.

TABLE 2

Reduced adsorption of carbon tetrachloride on TK800 samples dehydrated at various temperatures

Relative pressure P/P_0	Number of monolayers V/V_m			
	Sample <i>T</i> (290): BET-C \approx 18–19 *	Sample <i>T</i> (200): BET-C \approx 36–37	Sample <i>T</i> (380): BET-C \approx 4–5	Reference data [4] BET-C \approx 4–32
0.05	0.62	0.66	0.25	0.52
0.10	0.82	0.88	0.38	0.81
0.15	0.93	1.00	0.50	1.01
0.20	1.03	1.22	0.63	1.11
0.25	1.24	1.38	0.75	1.26
0.30	1.55	1.49	0.94	1.41
0.35	(1.85)	1.60	1.06	1.61
0.40	(2.27)	1.77	1.25	1.76
0.45	(2.58)	1.93	1.50	1.91
0.50	(2.99)	2.10	1.88	2.22
0.55	(3.40)	2.38	2.19	2.52
0.60	(3.91)	2.60	2.50	2.87
0.65	(4.53)	2.87	2.81	3.22
0.70	(5.07)	3.20	3.19	3.73
0.75	(6.28)	3.70	3.69	4.33
0.80	(7.42)	4.31	4.31	5.04
0.85	(9.27)	5.25	5.25	5.94
0.90	(12.57)	6.74	7.25	7.05
0.95	(24.72)	9.12	12.88 **	8.96
1.00	(43.26)	13.92	22.60 **	13.59

* Values in parentheses are V/V_m values involving multilayer adsorption and capillary condensation.

** V/V_m values involving only intergranular capillary condensation.

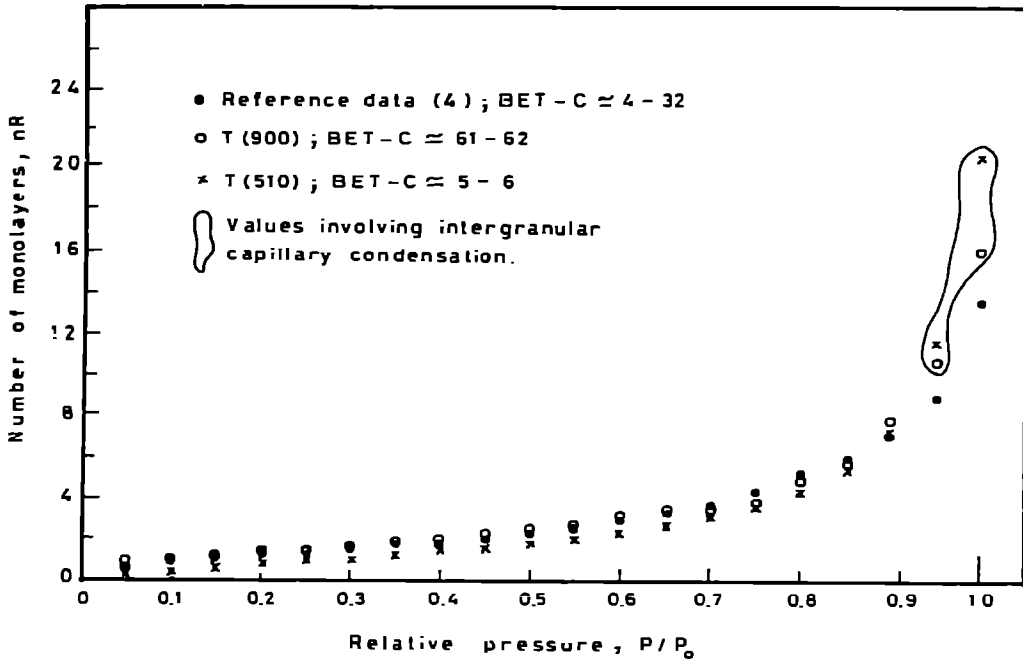


Fig. 2. The increased adsorption, V/V_m , vs. the enhanced BET-C values for some selected TK800 samples.

TABLE 3

Statistical number of monolayers for carbon tetrachloride adsorption on some selected TK800 samples

Relative Pressure P/P_0	Number of Monolayers, V/V_m		
	Reference data [4] BET-C \approx 4-32	Sample T(900): BET-C \approx 61-62	Sample T(510): BET-C \approx 5-6
0.05	0.52	0.76	0.29
0.10	0.81	0.94	0.46
0.15	1.02	1.08	0.61
0.20	1.11	1.18	0.80
0.25	1.26	1.31	0.92
0.30	1.41	1.43	1.03
0.35	1.61	1.68	1.20
0.40	1.76	1.85	1.37
0.45	1.91	2.07	1.49
0.50	2.22	2.22	1.68
0.55	2.52	2.42	1.91
0.60	2.87	2.76	2.18
0.65	3.22	3.05	2.52
0.70	3.73	3.40	2.98
0.75	4.33	3.84	3.63
0.80	5.04	4.68	4.29
0.85	5.94	5.81	5.44
0.90	7.05	7.69 *	7.10
0.95	8.96	10.74 *	11.68 *
1.00	13.59	16.06 *	20.61 *

* V/V_m values involving measurable intergranular capillary condensation.

Figure 2 illustrates the different V/V_m vs. P/P_0 curves for samples $T(510)$: BET-C \approx 5–6, $T(900)$: BET-C \approx 61–62 and the reference data [4]: BET-C \approx 4–32.

Sample $T(510)$: BET-C \approx 5–6 represents a special behaviour of minimum V/V_m values starting from the lower pressures and continuing to a relative pressure $P/P_0 = 0.85$.

On comparing the V/V_m vs. P/P_0 curves for sample $T(900)$, BET-C \approx 61–62, and the reference data [4], BET-C \approx 4–32, a substantial increase in V/V_m values and also in the relative pressure (P/P_0) is noted when the magnitude of the BET-C constant is increased. As is evident, sample $T(900)$ assumes higher V/V_m values which continue to a relative pressure $P/P_0 = 0.85$.

For both the samples $T(510)$ and $T(900)$, at relative pressures above $P/P_0 = 0.85$, the occurrence of marked intergranular capillary condensation is evident, and consequently the values of V/V_m at higher relative pressures ($P/P_0 > 0.85$) have already been reproduced [1,14] from sample $T(200)$, cf. Table 2. Different V/V_m values for these samples are listed in Table 3.

On comparing the V/V_m values and molecular adsorption values (S in $\mu\text{mole m}^{-2}$) for both the samples $T(380)$: BET-C \approx 4–5 and $T(510)$: BET-C \approx 5–6, as depicted in Table 4, the finite changes in V/V_m values at intermediate pressures were averaged — without detectable approximation — in a uni-

TABLE 4

Number of monolayers, V/V_m , and molecular adsorption of carbon tetrachloride for the samples $T(380)$ and $T(510)$

P/P_0	Sample $T(380)$		Sample $T(510)$	
	V/V_m	$S(\mu\text{mole m}^{-2})$	V/V_m	$S(\mu\text{mole m}^{-2})$
0.05	0.25	1.38	0.29	1.58
0.10	0.38	2.08	0.46	2.53
0.15	0.50	2.77	0.61	3.36
0.20	0.63	3.46	0.80	4.44
0.25	0.75	4.15	0.92	5.07
0.30	0.94	5.19	1.03	5.70
0.35	1.06	5.88	1.20	6.65
0.40	1.25	6.92	1.37	7.60
0.45	1.50	8.30	1.49	8.24
0.50	1.88	10.37	1.68	9.31
0.55	2.19	12.10	1.91	10.58
0.60	2.50	13.83	2.18	12.04
0.65	2.18	15.56	2.52	13.94
0.70	3.19	17.63	2.98	16.47
0.75	3.69	20.40	3.63	20.08
0.80	4.31	23.86	4.29	23.76
0.85	5.25	29.04	5.44	30.09
0.90	7.25	40.11	7.10	39.28
0.95	12.88 *	71.23	11.68 *	64.62
1.00	22.00 *	121.71	20.61 *	114.04

* V/V_m values involving measurable intragranular capillary condensation.

fied set of n_R -values representing the low BET-C values (4–6), which are listed in the second column of Table 5.

As graphically represented in Fig. 3, the infinitesimal changes in amount adsorbed (S in $\mu\text{mole m}^{-2}$) at some intermediate pressure 0.45–0.75 P/P_0 might reflect finite changes in the extent of multimolecular adsorption. The reduced adsorption values, V/V_m , at high relative pressures ($P/P_0 > 0.90$) was initially reproduced from sample $T(200)$, instead of from separate sample behaviours, which appears to contain predominantly measurable intergranular capillary condensation.

Based on previous measurements, reference n_R vs. P/P_0 curves were established, which represent several limited ranges of magnitude of the BET-C constant, namely 4–6, 15–19, 56–37 and 61–62. The newly developed sets of n_R were re-plotted separately as a function of relative pressure (P/P_0) as shown in Fig. 4.

The reduced adsorption values, n_R , are listed in Table 5. Finally, the t -values were easily calculated by multiplying the statistical number of monolayers, n_R , by the unilayer thickness t_m .

Preliminary application of recent n_R vs. P/P_0 curves on some aerosils provides a reliable measure of S_t -values, showing a good agreement with the surface areas calculated using the BET-method.

TABLE 5

Reference n_R values for carbon tetrachloride adsorption measurements

Relative pressure P/P_0	n_R * values			
	Sample $T(380)$ Sample $T(510)$: BET-C \approx 4–6	Sample $T(290)$ Sample $T(480)$: BET-C \approx 15–19	Sample $T(200)$: BET-C \approx 36–37	Sample $T(900)$ BET-C \approx 61–62
0.05	0.27	0.62	0.66	0.76
0.10	0.42	0.82	0.88	0.94
0.15	0.56	0.93	1.00	1.08
0.20	0.72	1.03	1.22	1.18
0.25	0.84	1.24	1.38	1.31
0.30	0.99	1.55	1.49	1.43
0.35	1.13	1.60	1.60	1.68
0.40	1.31	1.77	1.77	1.85
0.45	1.50	1.93	1.93	2.07
0.50	1.78	2.10	2.10	2.22
0.55	2.05	2.38	2.38	2.42
0.60	2.34	2.60	2.60	2.76
0.65	2.67	2.87	2.87	3.05
0.70	3.09	3.20	3.20	3.40
0.75	3.69	3.70	3.70	3.84
0.80	4.30	4.31	4.31	4.68
0.85	5.35	5.25	5.25	5.81
0.90	7.18	6.74	6.74	7.05
0.95	9.12	9.12	9.12	9.12
1.00	13.92	13.92	13.92	13.92

* Unilayer thickness $t_m = 5.30 \text{ \AA}$ for cross-sectional area $\sigma = 30 \text{ \AA}^2$, $t_m = 6.40 \text{ \AA}$ for cross-sectional area $\sigma = 25 \text{ \AA}^2$.

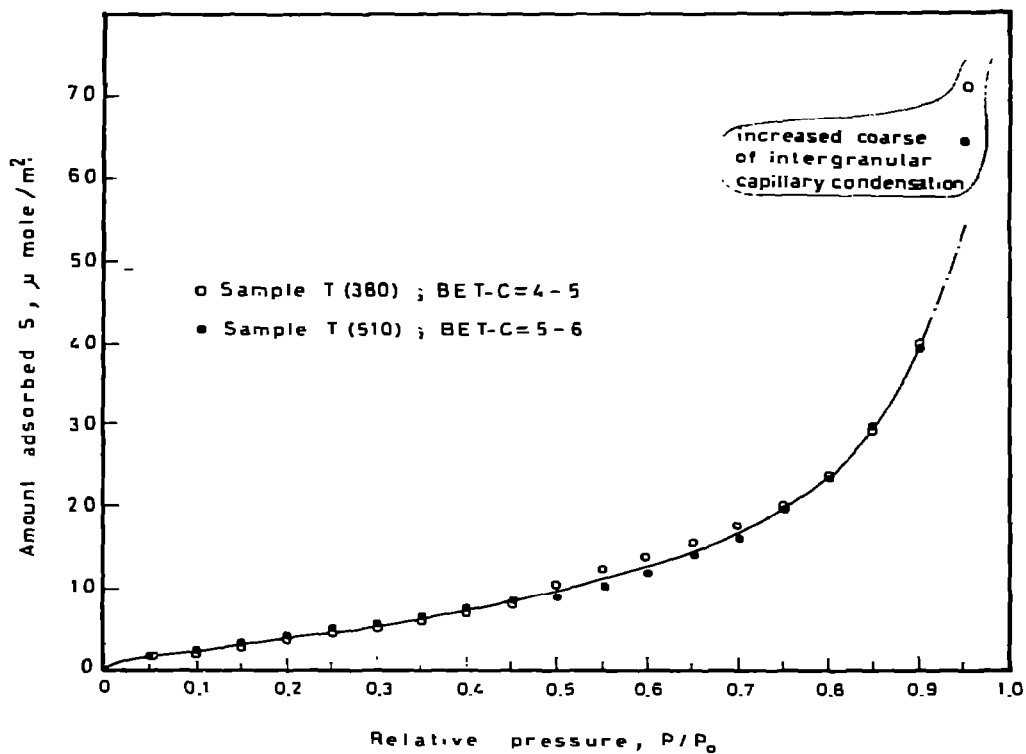


Fig. 3. Molecular adsorption isotherms (S in μ mole m^{-2} , P/P_0) for the samples $T(380)$ and $T(510)$.

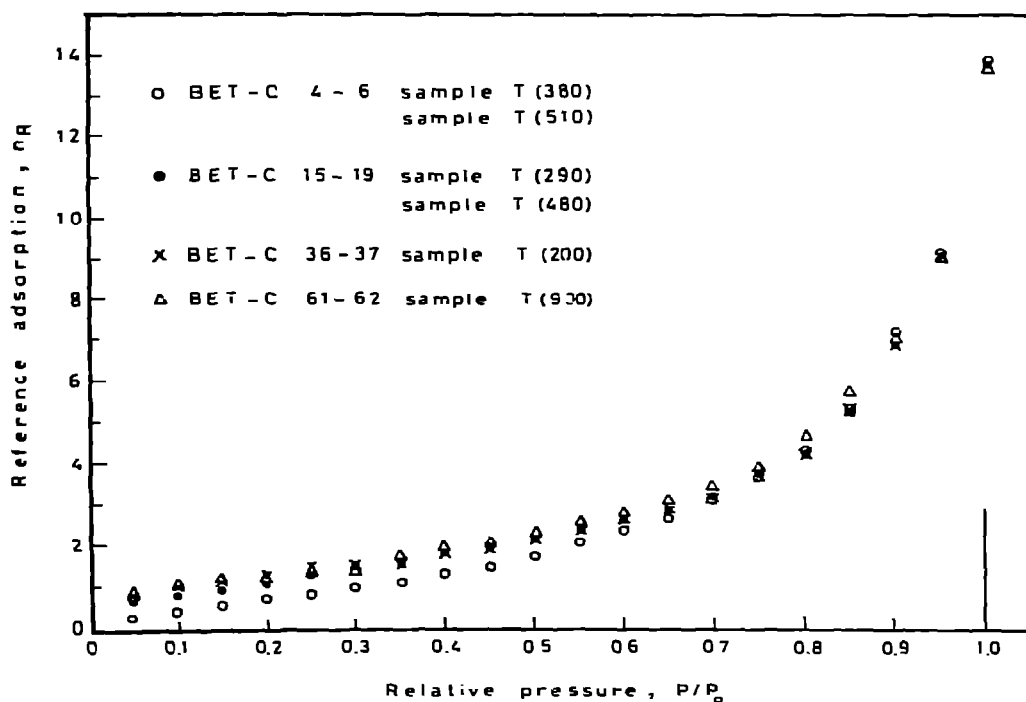


Fig. 4. Reference n_R vs. P/P_0 curves for carbon tetrachloride adsorption.

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