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ADSORPTION ISOTHERMS OF WATER ON A SET OF FRACTOSILS AND ON AVICEL PH 101^R BY FRONTAL ANALYSIS CHROMATOGRAPHY

Ho Nam-Tran*, Vo Van Nhuan, Michel Buchmann, Fouad Sabra, Paul Ruelle, Ulrich W. Kesselring
Institut d'Analyse pharmaceutique, Ecole de pharmacie, Université de Lausanne, CH-1015 Lausanne, Switzerland

SUMMARY

Residual water adsorbed on the surface of solids can modify significantly e.g.: stability of solids, properties of colloidal systems, compressibility of powders, oxidation phenomena, heterogeneous nucleation in the atmosphere, and may serve as a medium, favourable for the growth of numerous micro-organisms.

The aim of this work is the characterization, by physical and thermodynamic parameters, of adsorbed water on the surface of a set of Fractosils and of Avicel PH 101^R. Frontal analysis chromatography is used for the determination of adsorption isotherms. The analysis of the thermodynamic parameters of adsorbed water indicates that the water adsorption is either mobile or localized depending on the nature of the solids. The adsorbed water exists under three states: strongly bonded (up to the monolayer), weakly bonded and free (condensed water).

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* To whom correspondence should be addressed.

INTRODUCTION

Almost all of the organic solids, used in the pharmaceutical field as drugs, excipients, and carrier vectors, adsorbe water.

The amount of adsorbed water depends on the working temperature, the relative humidity of the environnement, and on the physico-chemical nature and structure of their surfaces.

Being very polar, adsorbed water has an important effect on the chemical stability of solids in the state[1-4], and mixtures[5-12], but also on the desintegration properties of tablets[13-16], the bio-availability and threfore on the therapeutic efficiency[17] of drugs.

In order to understand the role played by adsorbed water in the various processus, ways must be found to quantify it by measurable parameters. This quantification is difficult for two reasons: the choice of a reliable quantitative experimental method for the exact determination of the amount of adsorbed water and the lack of correct models for the data treatment yielding the desired parameters.

The determination of adsorption isotherms by gas-solid chromatography seems to be appropriate as it yields the amount of adsorbed water in the normally used domain of temperature and relative humidity, as well as information on the energy state of water adsorbed and the characteristics of the adsorbent surface[18]. With respect to other techniques (e.g. gravimetric methods with a micro-balance[19], or with quartz springs of Mac Bain Baker's type[20]) gas-solid adsorption chromatogaphy, being a dynamic method, is often faster than static methods[21], in that it yields results for a wide range of temperature and humidity without other technical complications[22-23].

Frontal analysis chromatography was introduced by James and Philipps[24], and Schay and Szekely[25], on the basis of the fundamental works of Glueckauf[26] and Beebe[27]. Some special technical features afterwards have been evidenced by Chauchard and Chabert[28] in their work about the water adsorption on the surface of ethylen-glycol-polyterephtalate and of polyamid 6,6. They came to the following interesting conclusions:

1. Adsorption-desorption equilibrium can be controled with frontal analysis.

2. The results obtained by gas chromatography deviate from those given by gravimetric methods to an extent of about 2.5%.

3. Because of the slow diffusion of water molecules into the solid mass, true equilibrium at high relative humidity is not easily reached, and the amount of adorbed water is (normally) underestimated.

Among the mathematical models proposed for description and calculation of adsorption isotherms from gas-solid chromatography, the most frequently used are Guggenheim-Anderson-de Boer[29-31], referred to as the G.A.B., and Hailwood-Horrobin[32] models.

The aim of the present paper is firstly to suggest the construction of a sample conditioning device (e.g. a saturation system coupled with a chromatographe) for the determination of the water adsorption isotherms on Avicel PH 101^R and some Fractosils (e.g. amount water adsorbed by 1 gr of adsorbent, r(g/g), as a function of the relative humidity, p/p_o, and of the temperature T(K).

Secondly, for the purpose of quantification of the states of adsorbed water, different physical and thermodynamic parameters are calculated from the data of the determined adsorption isotherms such as:

- The specific area with respect to the water, Σ_{H2O}, as well as the molar net heat of adsorption at the monolayer, $(\Delta_{ads}H_1 - \Delta_L H)$, and at intermediate layers, $(\Delta_{ads}H_m - \Delta_L H)$.
- Different constants of the models used.
- The entropic adsorption constant, Z, proposed as an indication of adsorbate mobility[33].
- The variation of the isosteric enthalpy, isosteric entropy and isosteric free enthalpy as a function of the degree of coverage, Θ, expressed in number layers.

THEORETICAL

1. **Principle of frontal analysis chromatography.**

The principle of frontal analysis chromatography consists in letting the carrier gas (helium) circulate within the dry sample until the

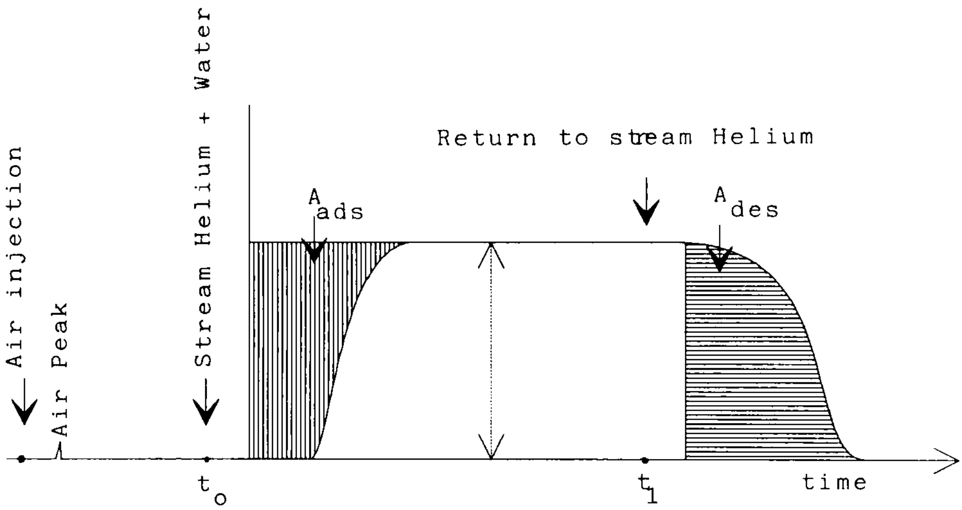


FIGURE 1

Frontal chromatographic diagram.

base line is stable. Then at time t_o, the carrier gas is replaced by a water-carrier gas mixture, which has exactly the same flow rate, D_s, and a concentration, c_s, in water. Adsorption equilibrium is reached, once the maximun height of the platform of the chromatogram no longer varies with time. At time t_1, the helium-water flow is replaced by pure carrier gas, and the desorption curve is complete when the base line is again reached. The hatched area, A_{ads}, is proportional to the quantity of water adsorbed by the sample, whereas the dotted area, A_{des}, is proportional to the quantity of water released from the sample during desorption. If the phenomenon is totally reversible, the two area, A_{ads}, and, A_{des}, must be equal (FIGURE 1).

The mass, r, of water adsorbed on the sample is calculated from the chromatographic conditions as well as from the characteristics of the chromatogram according to equation:

$$r = \frac{18\ D_s\ p_a\ p\ A_{ads}}{m\ v\ R\ h\ T_a\ p_c} \qquad [1]$$

where

r:= relative quantity of water adsorbed on the adsorbent (g/g)

D_s:= flow rate of the carrier gas (ml/min)

m:= mass of adsorbent in the column (g)

R:= perfect gas constant = 82.057 (cm atm K)

v:= chart paper rate (cm/min)

h:= height of chromatographic platform (cm)

p_a:= ambient pressure (atm)

T:= room temperature (K)

p_c:= pressure within the column (atm)

p:= partial pressure of water according to temperature tables (atm)[34]

A_{ads}:= adsorption surface (cm^2)

The adsorption isotherm at given temperature is obtained by plotting r vs p/p_o, p/p_o being the relative water vapor pressure.

$$p_c = \frac{p_s}{j} = \frac{p_e + p_s}{2} \quad [2]$$

$$j = \frac{3\,((p_e/p_s)^2 - 1)}{2\,((p_e/p_s)^3 - 1)} \quad [3]$$

$$p_s = 1 - 0.028 = 0.972 \quad [4]$$

p_e:= pressure at the entrance of the column (atm)

p_s:= pressure at the exit of the column, supposed to be close to atmospheric pressure, p_a.

j:= James and Martin's factor[35], introduced to correct the loss of charge in the column.

As p_s, is considered to be close to p_a, its value must be corrected with respect to the saturated vapour of soap water at the temperature of the soap bubble flowmeter. At 25°C the value to subtract is equal to 0.028 atm.

2. Short consideration of adsorption models

2.1 BRUNAUER-EMMETT-TELLER'S MODEL[36] (B. E. T.)

The B. E. T.'s model has the following mathematical expression:

$$\frac{p/p_o}{r(p/p_o)} = \frac{1}{C_B r_m} + \frac{C_B - 1}{C_B} p/p_o \qquad [5]$$

where

$$C_B = Z \exp - \frac{(\Delta_{ads}H_1 - \Delta_L H)}{RT} \qquad [6]$$

$$\sum = \frac{n_a}{m} a_m N_A 10^{-20} \qquad [7]$$

r_m: relative quantity of adsorbed adsorbate corresponding to a monolayer on the adsorbent (g/g)

C_B: B. E. T. constant

$\Delta_{ads}H_1$: adsorption enthalpy at the monolayer (kal/mol)

$\Delta_L H$: condensation heat of adsorbate (kcal/mol)

$\sum$: specific area of the adsorbent (m^2/g)

n_a: number of moles of adsorbed adsorbate in the monolayer

a_m: molecular projection area of the adsorbate (A^2)

m : mass of the adsorbent (gr)

N_A: Avogadro's constant ($6.02252 * 10^{23}$ mol^{-1})

$$\Delta_{ads}G_1 = -RT \, LnC_B \qquad [8]$$

$$\Delta_{ads}H_1 = \Delta_L H - RT \, Ln(C_B/Z) \qquad [9]$$

$$\Delta_{ads}S_1 = R \, LnZ + \Delta_L H/T \qquad [10]$$

$$\Delta_L H = -\Delta_{vap}H \qquad [11]$$

$\Delta_{ads}G_1$: free adsorption enthalpy at the monolayer (kal/mol)

Δ_{vap}: vaporisation enthalpy (kal/mol)

$\Delta_{ads}S_1$: adsorption entropy at the monolayer (cal/mol K)

$$\Delta_{vap}H = 12.08 - 0.006507 \, T \qquad [12]^{37}$$

$Z = \exp(\Delta_{ads}S_1 - \Delta_L S)/R$ is an entropic adsorption factor, the value of which is obtained by calculating the $\Delta_{ads}H_1$ as a function of Z varying between 10^{-5} (very localized adsorption) and 10 (very mobile adsorption)[33]. The obtained values of $\Delta_{ads}H_1$ are then compared with the isosteric adsorption enthalpy at the monolayer, $\Delta_{ads}H_{isost}$,

calculated by normal themodynamic method (see equation [21])
The coincidence between the values derived from two methods allows to situate the true value of Z.

2.2 GUGGENHEIM-ANDERSON-de BOER'S MODEL (G. A. B.)[29-31]

The G. A. B.'s model is similar to B. E. T.'s model (equation [5]), except for the addition of third parameter, K; it was derived to take into account layers of adsorbed water having properties intermediate to those in the first layer and those of bulk water. The following expression results:

$$(p/po)r = \frac{1}{r_m C_G K} + \frac{(C_G - 2)}{r_m C_G}(p/po) - \frac{(C_G - 1)K}{r_m C_G}(p/po)^2 \qquad [13]$$

The constants, C_G, and, K, can be determined as

$$C_G = D\exp\left(-\frac{(\Delta_{ads}H_1 - \Delta_{ads}H_m)}{RT}\right) \qquad [14]$$

$$K = B\exp\left(-\frac{(\Delta_{ads}Hm - \Delta_L H)}{RT}\right) \qquad [15]$$

Where, D, B = 1, are constant, $\Delta_{ads}H_m$ is the heat of adsorption of water in the intermediate layers.
Furthermore, the following equations may be derived from the above equations:

$$C_G/(K\ D) = \exp\left(-\frac{(\Delta_{ads}H_1 - \Delta_L H)}{RT}\right) \qquad [16]$$

$$D = (Z\ C_G)/(C_B K) \qquad [17]$$

$$RT\ Ln(C_G/K\ D) = \Delta_{ads}H_1 - \Delta_L H \qquad [18]$$

$$RT\ Ln\ K = \Delta_{ads}H_m - \Delta_L H \qquad [19]$$

Using the values of Z, C_G, C_B, K, the net heats of adsorption, $(\Delta_{ads}H_1 - \Delta_L H)$, $(\Delta_{ads}H_m - \Delta_L H)$, and the constant, D, are easily calculated (eq. 17, 18, 19).

2.3 **Hailwood-Horrobin's model**[32]

Hailwood-Horrobin worked out a special model for water-sorption on fibrous polymers (Cotton, Wool, Silk). The underlying hypotheses imply:

a) formation of a solid-water solution in polymers.

b) fixing of water to form hydrates (bound water) which is in equilibrium with the rest of the water retained on the polymer fibre (free water). Assuming that the components (bound water, free water, polymer fraction ill opened to water vapour) form an almost ideal solution, Hailwood and Horrobin proposed the following relationship:

$$(H\ 100/r) = A + B\ H - CH^2 \qquad [20]$$

Where

$$A = \frac{m_p}{1800\ (1+\beta)\ \alpha}$$

$$B = \frac{m_p\ (\beta - 1)}{1800\ (1+\beta)}$$

$$C = \frac{\alpha\ \beta\ m_p}{1800\ (1+\beta)}$$

$$\alpha = \frac{-B + (B^2 + 4\ A\ C)^{1/2}}{2\ A}$$

$$\beta = \frac{C}{A\ \alpha^2}$$

$$m_p = 1800\ \alpha\ (1+\beta)\ A$$

$$r_m = \frac{1}{1800\ \alpha\ (1+\beta)\ A}$$

m_p: mass of polymer able to fix one mole of water as hydrate (g)

α: equilibrium constant, water vapor – free water

β: equilibrium constant, hydrate - polymer fraction available for water adsorption + free water

H:= (100 p/po, % relative humidity)

3. **The thermodynamic equations[38] to compute isosteric quantities (isosteric enthalpy, $\Delta_{ads}H_{isost}$, isosteric entropy, $\Delta_{ads}S_{isost}$, isosteric free enthalpy, $\Delta_{ads}G_{isost}$) of adsorption are the following:**

$$(\mathrm{Ln}\ p)_\Theta = \frac{-\Delta_{ads}H_{isost}}{RT} + \mathrm{Constant} \qquad [21]$$

$$\Delta_{ads}S_{isost} = \frac{\Delta_{ads}H_{isost}}{R} - R\,(\mathrm{Ln}\ p/p_o)_\Theta \qquad [22]$$

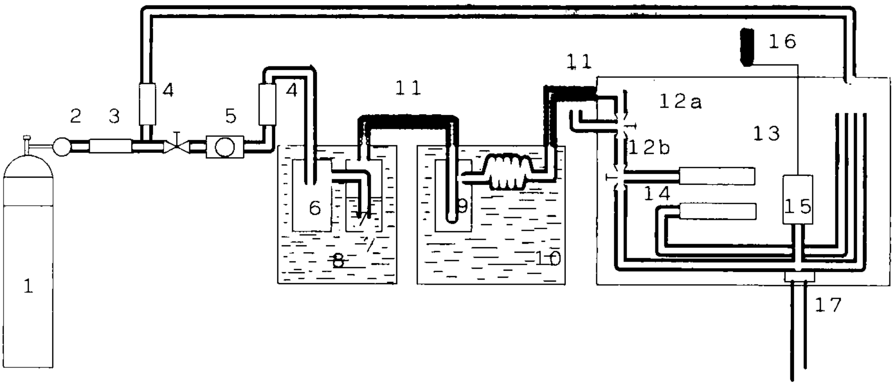
$$\Delta_{ads}G_{isost} = \Delta_{ads}H_{isost} - T\,\Delta_{ads}S_{isost} \qquad [23]$$

The value of, $\Delta_{ads}H_{isost}$, computed according to equation [21] at the monolayer will be taken as a reference to situate the value of Z calculated according to equation [6].

EXPERIMENTAL

Conditioning device

For the determination of water isotherms by gas-chromatography, it is necessary to know precisely the partial water vapor pressure in the carrier gas. This is quite easily obtained by saturating the carrier gas with water at desired temperature. All what is needed are two high precision thermostats (±0.1°C), and a home made saturation unit to assure a constant helium-water flow at the predetermined partial water pressure. The whole device is coupled to a Hewlett-Packard chromatograph, series 5880A, equiped with a thermic detector TCD and an integrator of the same series(FIGURE 2).



1. Pure Helium gas
2. Reducing valve
3. Purifying trap
4. Flow rate regulator
5. Pressure regulator
6. Anti-reflux security
7. Bubler(containing water)
8. Oil bath(maintained at temperature higher than that of the columns)
9. Condenser
10. Thermostat(± 0.1°C)
11. Heating element
12. Three way valves
13. Gas-chromatograph
14. Columns
15. Thermal conductivity detector
16. Soap flowmeter
17. Signal

FIGURE 2

Block scheme of saturation system connected to gas-chromatograph.

The carrier gas is helium (Carbagas, purity > 99.99 %), its pressure at the exit of the helium source is controlled by a pressure-reducer[a] (2 on the block scheme). Eventual residual oxygen in the carrier gas is removed by a molecular sieve[b] (3). At the exit of molecular sieve, the helium is led into two different cycles, the flow rates beeing kept constant by two flow rate regulators[c] (4) and by a Wilkerson's pressure regulator[d] (5). The

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[a] pressure reducer
[b] catalyser R 3-11 (No 18820), Fluka AG, CH-9470 Buch
[c] Wisag, model 1100, KDG flowmeter, Creydon RA 629679, CH-8057 Zuric
[d] Wisag, Willoughby Ottio, No 44094, CH-8057 Zurich

flow rate is measured at the exit of the chromatograph with a soap flowmeter (16).

The reference cycle is permanently supplied with pure, dryed helium. The gas flow of the sample cycle passes first the saturation chamber (7) then. Two three-way valves[e] (12) permit to send either pure helium or a helium-water mixture into the working column. In order to keep the base line constant , the flow rates in the two cylces must be identical . The temperature of the thermostat (10) determines the partial pressure of the water vapour of the helium-water mixture. In varying the temperature of the thermostat bath (10), it is possible to obtain relative humidities ranging from 0.5 up to 99%.

Sample treatment

First of all the samples are dried by flushing them with pure helium for 48 hours at 80°C. Then the heliumm stream with exactly known flow rate and entrance pressure, p_e, at working temperature the two columns until the base line is passed through stable. The pressure is regulated (5) such that the working column entrance pressure, p_e, is equal to the pressure at the injector. The pressure gradient, Δp, between the entrance pressure , p_e, and the pressure at the injector is measured with a manual manometer having a dial and a probe needle. The relationship between p_e, and p_s (eq. 4) is following:

$$p_e = p_s + \Delta p \qquad [24]$$

The flow rate of the working column is monitored with a valve (12) equiped with a small draining to relaxe the helium-water flow. At time, t_o, when the flow rates in the two cycles are identical, the valve (12b) is opened and the helium-water flow passes into the working column. When the adsorption equilibrium is reached, at time,

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[e] Wisag, Whitey, model SS-42 F_2, CH-8057 Zurich

t_1, (i.e. when the platform of the chromatogram no longer varies with time), the helium-water flow is replaced by pure helium for desorption (valve 12b turned off).

Materials

Fractosil^R (200, 1000, 2500, 5000, 10000)[f] and Avicel[g] PH 101^R are used as received (TABLE 1)

Working conditions

Column length	8 - 36 cm
Internal and external diameters	5.4, 6.35 cm
Carrier gas	helium
P_e	≈ 1 atm
Working temperatures	40 - 70°C
Injector temperature	110°C

TABLE 1

Characterisation of Fractosil^R and Avicel PH 101^R

Substance	Batch Nr	Specific Surface Area, Σ (m^2/g)[h]		Mean Pore Diameter (nm)
		as manufacturer's indication	experimental values	as manufacturer's indication
Fractosil^R 200	TA 10080	150	95.28 ± 1.0 (n=12)	21
Fractosil^R 1000	CC 717884	20	18.7 ± 0.2 (n=12)	115
Fractosil^R 2500	YE 20764	8	15.3 ± 0.1 (n=12)	250
Fractosil^R 5000	YE 15265	3	6.1 ± 0.1 (n=10)	500
Fractosil^R 10000	YE 300166	1.5	2.2 ± 0.04 (n=10)	1100
Avicel PH 101^R			1.3 ± 0.09 (n=10)	10.2

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[f] E. Merck, D-6100 Darmstadt 1

[g] Fluka AG, CH-9470 Buchh

[h] from B. E. T. nitrogen adsorption isotherms

Detector temperature	120°C
Filling mass	0.8 - 5 gr
Flow rate	(50 ± 1) cm^3/min

The columns were filled according to the Tranchant[37] technique.

RESULTS AND DISCUSSION

1. Water Adsorption Isotherms of five Fractosils and Avicel PH 101 .

At low relative humidity, water isotherms of Fractosil^R 5000 may be established by elution gas chromatography (FIGURE 3). Above about 30% rh, the thermodynamic equilibrium is not attained in the column for elution gas chromatography and frontal gas-solide chromatography becomes more convenient (FIGURE 3).

The experimental data of water isotherms of Fractosil^R 5000 at 60°C (FIGURE 4) and of Avicel PH 101^R at 60°C (FIGURE 5) are evaluated and represented according to the three mentionned models:

At low relative humidities up to 35%, the three models considered fit well the experimental points, beyond this limit the divergence becomes substantial. Then the B. E. T. fitting curve approaches the infinity, as 100 p/p_o approaching 100%; whilst the G. A. B. and the Hailwood-Horrobin models can both be used indiscriminately.

Some points concerning the influence of the temperature on the isotherms of water on Fractosil^R 5000 (FIGURE 6) and on the Avicel PH 101^R (FIGURE 7) may be mentionned:

There is a affinty between each set of graphs, and these adsorption isotherms are considered as a type II according to the Brunauer-Deming-Teller classification[40]. In the case of Fractosil^R 5000, variations of amounts of adsorbed water do not seem be a function of the temperature; whereas a significant variation of amounts of adsorbed water is observed in the case of Avicel PH 101^R. The observed graphs of the last case are similar to those published by Nakai[41], Hollenbeck[42], Zografi[43-44] and Sadeghnejad[45].

The run of adsorption isotherms of water on Fractosils^R depend on their specific area and or on their porosity. Mesoporous Fractosil^R 200, having the largest specific area with nitrogen, adsorbs a larger amount of water than other Fractosils^R (FIGURE 8).

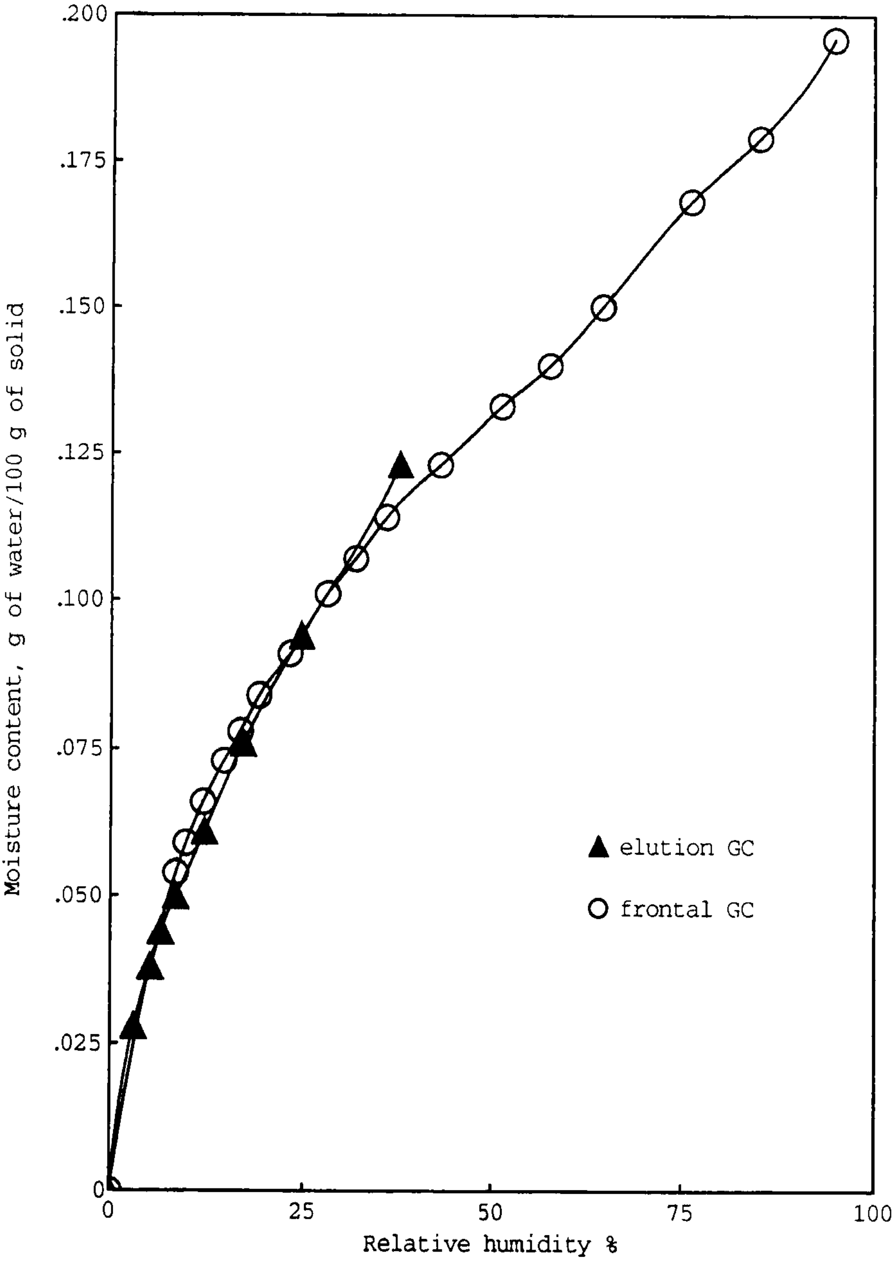

FIGURE 3

Two methods for adsorption isotherms of water on Fractosil^{R} 5000 at 40°C.

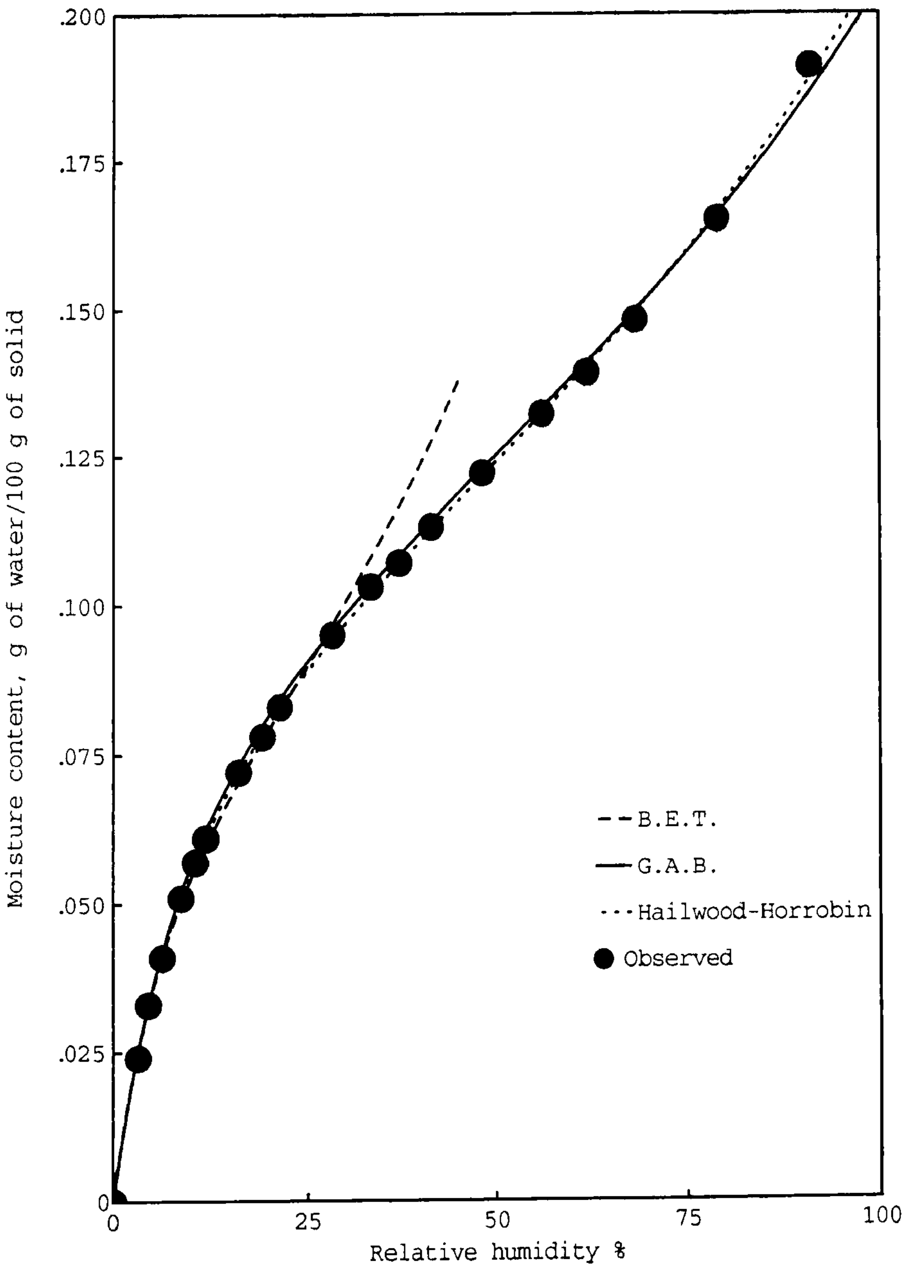

FIGURE 4

Adsorption isotherm of water on Fractosil^{R} 5000 at 60^{o}C.

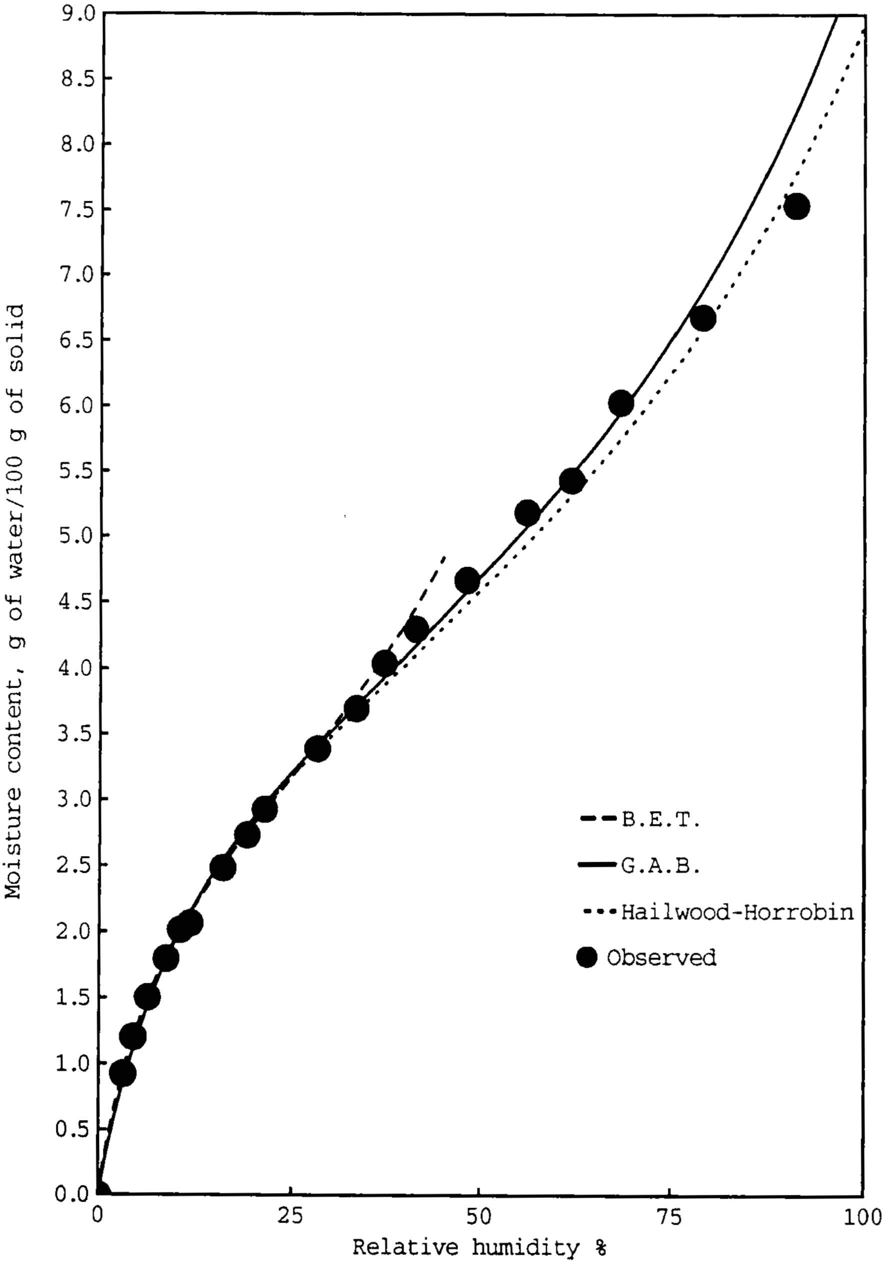

FIGURE 5

Adsorption isotherm of water on Avicel PH 101^{R} at 60°C.

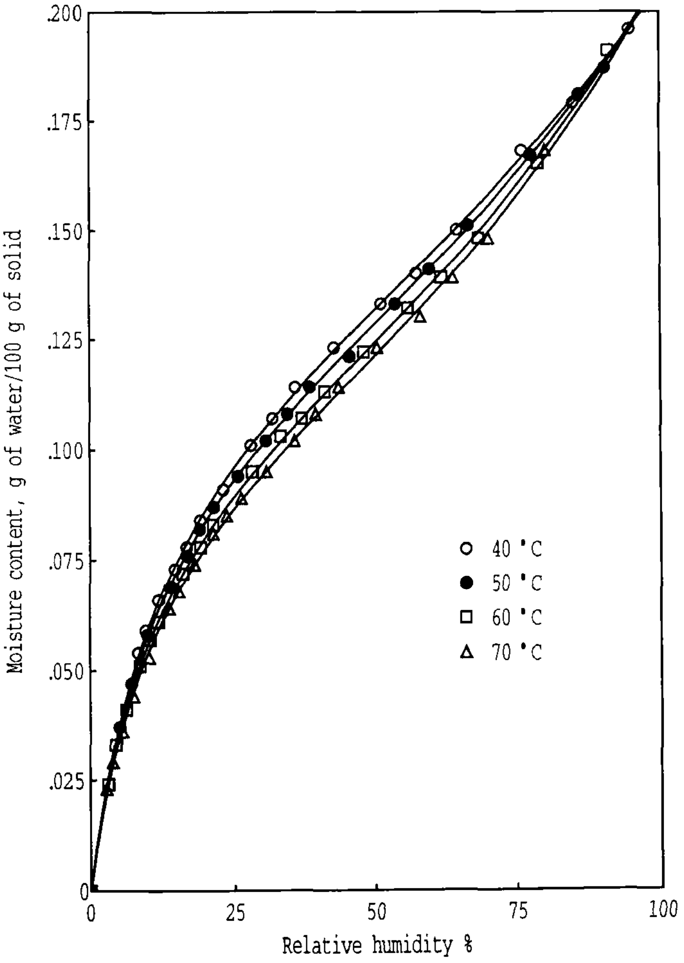

FIGURE 6

Adsorption isotherms of water on Fractosil^R 5000 at different temperatures. Fitted curves according to Hailwood-Horrobin's model.

2. Estimated values for parameters of used adsorption models.

The amount of adsorbed water at the monolayer depends on the models used (TABLE 2), and decreases, when porosity increases (TABLE 1). Hovever a large amount of adsorbed water for Avicel PH 101^R was observed. It is worth-while to notify that the values, r_m, must be

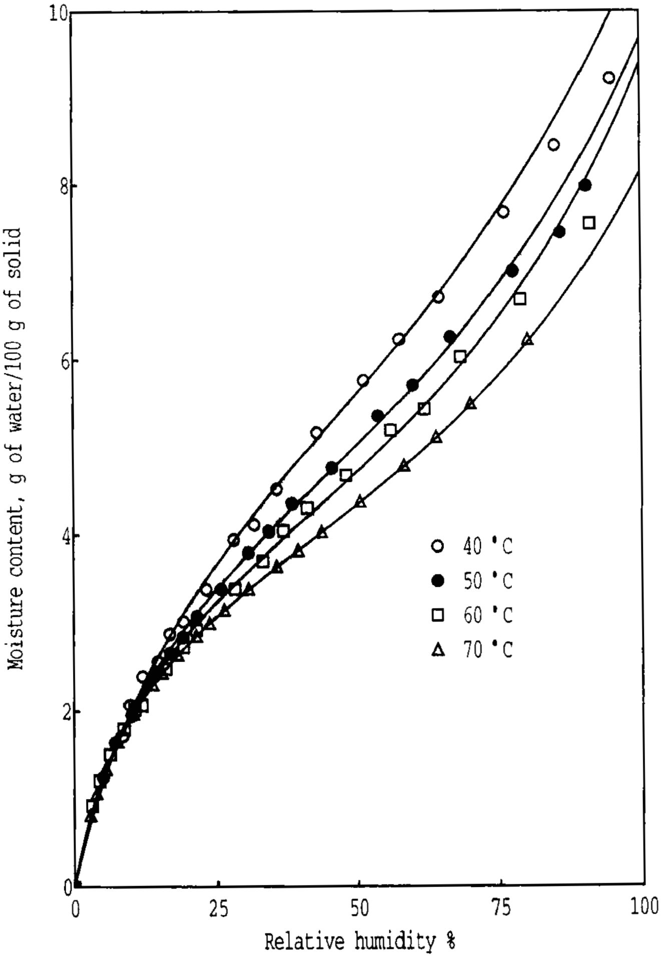

FIGURE 7

Adsorption isotherms of water on Avicel^{R} at different temperatures. Fitted curves according to Hailwood-Horrobin's model.

taken with precaution, if they have been estimated fron the linear form of the B. E. T.'s model. According to Gregg and Sing[46], this linearness has little signification, when the isotherm is of type II and slightly sigmoid, i.e., the estimated value of the constant, C_B, is smaller than 50. In this work , the value of, r_m, for Avicel PH 101^{R} is (0.034 (g/g)) at 40°C and very close to that found by

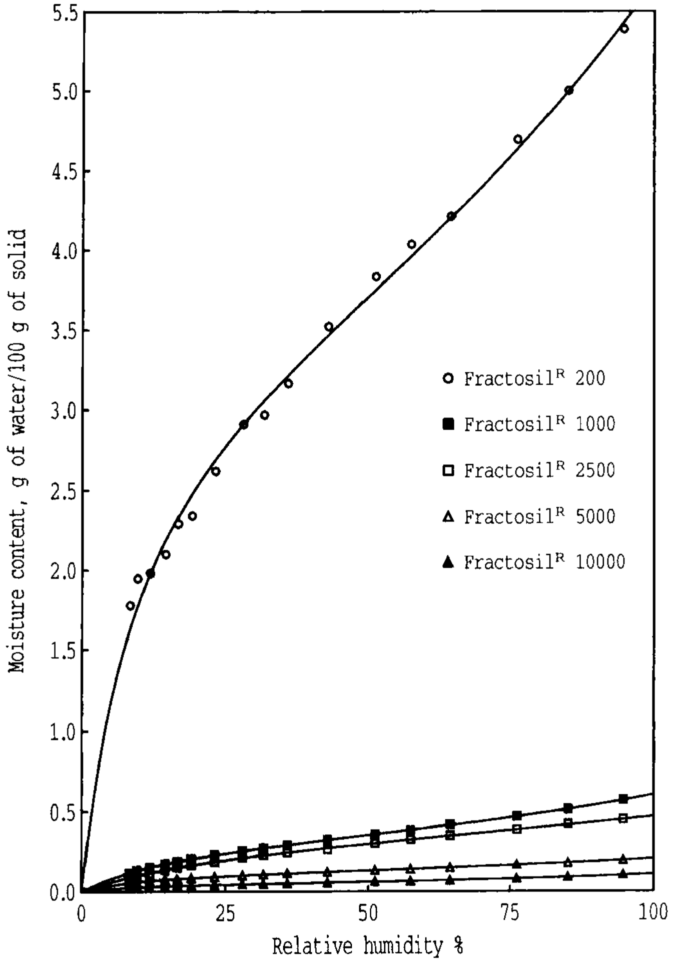

FIGURE 8

Adsorption isotherms of water on set of Fractosils^R and on Avicel PH 101^R.

Hollenbeck[42] (0.038 (g/g)) at 25°C, Nakai[47] (0.035 (g/g) at 35°C). For the different solids, the amount of adsorbed water decreases as temperature increases (TABLE 3). This corresponds to the nature of the physical adorption, and the dilatation of adsorbat at high temperature.

TABLE 2

Amount Of Water Adsorbed At The Monolayer, Calculated According To The Three Models: B. E. T., G. A. B., And Hailwood-Horrobin At 40°C

	10^3 r_m (g/g)		
Substance	B. E. T.	G. A. B.	Hailwood-Horrobin
Fractosil^R 200	22.00 ± 0.6	31.0 ± 1.0	33.0 ± 6.0
Fractosil^R 1000	2.26 ± 0.07	3.50 ± 0.2	3.5 ± 0.50
Fractosil^R 2500	2.03 ± 0.09	3.30 ± 0.10	3.3 ± 0.10
Fractosil^R 5000	0.87 ± 0.013	1.16 ± 0.02	1.16 ± 0.08
Fractosil^R 10000	0.369 ± 0.003	0.470 ± 0.001	0.48 ± 0.03
Avicel PH 101^R	34.5 ± 1.2	50.0 ± 2.0	54.0 ± 1.10

TABLE 3

Influence Of Temperature, On Adsorbed Water At The Monolayer, r_m, Calculated According To Hailwood-Horrobin's Model.

Substance	$10^3 r_m$ (g/g)			
	40°C	50°C	60°C	70°C
Fractosil^R 200	33.0 % 6.0	32.0 % 5.0	26.0 % 4.0	24.0 % 3.0
Fractosil^R 1000	3.5 ± 0.5	2.8 ± 0.2	2.8 ± 0.3	2.9 ± 0.3
Fractosil^R 2500	3.3 ± 0.1	2.9 ± 0.2	2.7 ± 0.3	2.7 ± 0.3
Fractosil^R 5000	1.1 ± 0.8	1.1 ± 0.3	1.1 ± 0.3	1.03 ± 0.80
Fractosil^R 10000	0.48 ± 0.03	0.46 ± 0.04	0.43 ± 0.04	0.38 ± 0.03
Avicel PH 101^R	54. ± 11	45. ± 7	39. ± 6	35. ± 5

TABLE 4

Values Of The Specific Area, Σ_{H2O}, Of Different Solids According To The Three Models: B. E. T., G. A. B., And Hailwood-Horrobin At 40°C

Substance	Σ_{H2O} (m^2/g)		
	B. E. T.	G. A. B.	Hailwood-Horrobin
Fractosil^R 200	78.5 ± 2.0	109.0 ± 3.5	117.0 ± 21.0
Fractosil^R 1000	8.01 ± 0.24	12.4 ± 0.7	12.4 ± 1.7
Fractosil^R 2500	7.19 ± 0.31	11.7 ± 0.3	11.7 ± 0.3
Fractosil^R 5000	3.1 ± 0.04	4.1 ± 0.07	4.1 ± 0.3
Fractosil^R 10000	1.31 ± 0.01	1.6 ± 0.003	1.7 ± 0.1
Avicel PH 101^R	122 ± 4.2	177.0 ± 7.1	191.0 ± 3.9

In adsorption, many problems arise from the estimated specific area. Indeed, the specific area is estimated from the amount, r_m, of adsorbed water at the monolayer which depends on the used models (TABLE 2), and varies as a function of temperature (TABLE 3). Furthermore, according to Karnaukhov[48], the conformity cannot exist, becauce the specific area still depends on the shape of adsorbat and its projections. In the case of water, its projection, a_s, may vary between[49] 10.6 A^2 and 25 A^2. If the value 10.6 A^2 is chosen for, a_s, of water, the following specific area, Σ_{H2O}, of Fractosils^R and Avicel PH 101^R are obtained (TABLE 4) according to the three models used:

For Avicel PH 101^R, when the value of the molecular projection of water is 10.6 A^2 at 40°C, the specific area, Σ_{H2O}, would be 122. ± 4.2 (m^2/g). This value is different from those obtained by Nakai[41] (149 m^2/g at 35°C), and Hollenbeck[42] (138 m^2/g at 25°C). This divergence is partly due to the use of the value 12.5 A^2 instead of 10.6 A^2. Furthermore, in the case of Fractosils^R there is no great

TABLE 5

Values Of Different Parameters In Relation To Adsorption Heat For Different Models.

Parameter	Fractosil					
	200	1000	2500	5000	10000	Avicel PH 101^R
C_B	20.6±0.9	7.8±0.6	10.5±0.7	14.5±0.4	19.0±0.4	10.6±0.8
C_G	24.2±4.1	10.5±1.7	11.8±0.4	18.8±0.3	19.6±1.1	10.3±1.0
K	0.51±0.07	0.36±0.06	0.49±0.02	0.48±0.02	0.61±.03	0.56±.06
$10^3\alpha$	4.5±0.4	3.7±0.3	4.9±0.1	4.8±0.2	5.9±0.20	5.4±0.4
β	23.2±4.1	9.5±1.0	10.8±0.4	17.8±0.3	18.6±1.1	9.3±1.2
D	0.02±.005	0.4±0.01	0.2±0.02	2.7±0.10	1.7±0.10	0.2±.003

difference between the specific area determined by the adsorption of water or of nitrogen (TABLES 1, 4), but the difference is very large for Avicel. This fact suggests that the mechanism of adsorption is not the same for both categories of solids.

Using the above mentionned models, different parameters of adsorption were estimated and presented on TABLE 5.

The values of, C_B, and, C_G, are not very different. However, those of, C_G, are always larger than those of C_B.

The values of , K, are nearly constant and vary slightly between 0.36 and 0.61. According to Brunauer[50], the parameter, K, is defined as a measure of the attractive strength field of the adsorbant. They are furthermore related to the degree of coverage, θ, expressed in static number of adsorbed layers. When K approachs 1, the degree of coverage, θ, is very large and tends to infinity; when the last is lower than 5, K is about 0.79. In this study, the values of K are all lower than 0.79, therefore, the number of layers at saturation should be lower than 5 and around 3.

The constant, α, is the equilibrium constant between water vapour and condensed water. At such a stage, the potential strength field of the

TABLE 6

Values Of Constant, Z, Computed From Adsorption Isotherms At 40°C

Substance	Z	Nature of adsorption
Fractosil^R 200	10^{-2}	localized
Fractosil^R 1000	10^{-1}	localized
Fractosil^R 2500	10^{-1}	localized
Fractosil^R 5000	1	mobile
Fractosil^R 10000	1	mobile
Avicel PH 101^R	10^{-1}	localized

surface of adsorbent loses its importance, consequently, α must have more or less the same values, this was always observed.

The β, equilibrium constant between hydration water and fraction of solid not yet occupied + free water, depends on the state of hydration. The values of, β, give some idea about the adsorption behaviour of the solids.

The constant, D, is a function of the adsorption entropy of the first layer related to the second layer taken as reference. The smaller the value, the greater the difference of order between first layer and the intermediate are. This is the case with Fractosil^R 200 and with Avicel PH 101^R.

In order to have some idea about the mobility of adsorbed water on the mentionned solids, the values, Z, are listed in the TABLE 6. According to the obtained values of, Z, the localized adsorption is for Fractosils 200, 1000, 2500, and on Avicel PH 101^R, and is mobile for Fractosils 5000, 10000. These values are in accordance with that of, D, (TABLE 5).

3. Thermadynamic properties of adsorption

The energetic aspect of the surface of the solids studied may be determined by the net heats of adsorption at monolayer,

TABLE 7

Molar Net Heat Of Adsorption At The Monolayer And At The Intermediate Layers , According To G.A.B.'s Model At 40°C.

Substance	$-\lvert\Delta_{ads}H_1 - \Delta_L H\rvert$ (kcal/mol)	$-\lvert\Delta_{ads}H_m - \Delta_L H\rvert$
Fractosil^R 200	4.75±0.21	0.42±0.08
Fractosil^R 1000	2.71±0.21	0.60±0.10
Fractosil^R 2500	2.89±0.04	0.44±0.02
Fractosil^R 5000	1.67±0.04	0.46±0.03
Fractosil^R 10000	1.83±0.06	0.31±0.03
Avicel PH 101^R	2.90±0.13	0.36±0.07

($\Delta_{ads}H_1 - \Delta_L H$), and at intermediate layers, ($\Delta_{ads}H_m - \Delta_L H$). Their values are listed in TABLE 7.

Considering values of D (TABLE 5), it is obvious that $\lvert\Delta_{ads}H_1 - \Delta_L H\rvert > \lvert\Delta_{ads}H_1 - \Delta_{ads}H_m\rvert$ for all kinds of solids. Such a difference strengthens the hypothesis of the existence of intermediate layers.

The net heat of adsorption at the monolayer for Avicel PH 101^R is -2.9 kcal/mol. This value is nearly the same of that obtained by Hollenbeck[40] (-3.5 kcal/mol) using immersion calorimetry. However, this value is quite different from those given by Zografi[43] (-1.9 kcal/mol) and Hollenbeck[42] (-1.66 kcal/mol) using adsorption technique. Such differences may be explained by the fact that the constants D and Z are assumed equal to one by the last authors, and consequently, such values supposed constants do not correspond to the localized nature of adsorption (TABLE 6). In another way, by the thermodynamic method, the value of isosteric heat of adsorption for Avicel PH 101^R at the monolayer was obtained as -13.20 kcal/mol according to equation [21]. The different value between the above isosteric heat (-13.20 kcal/mol) and that of the heat of condensation (-10.05 kcal/mol) was -3.15 kcal/mol. This value nearly approaches the value -2.9 kcal/mol calculed by G.A.B's model.

Considering the two values (-2.9, -3.15 kcal/mol) and that of Hollenbeck[42] (-3.5 kcal/mol), the two values : -1.9, -1.66 kcal/mol seem to be low. However, the value -3.5 kcal/mol may be high, because of the added value of the heat of vaporisation produced at the moment of the breaking of the cell. Such a heat of vaporisation is inherent to immersion calorimetry[42], this problem is not resolved yet.

Considering the value of the isosteric heat of adsorption of water on Avicel PH 101^R at the monolayer, -13.2 kcal/mol, this value contains two contributions: dispersive and hydrogen bond . If the value -1.026 kcal/mol, calculated from dispersive partial parameters of these two partners ($\Delta_{ads}E = - V_1\delta_1\delta_2$)[51], is assigned to be dispersive contribution, then the part of hydrogen bonding of adsorption will be of -12.17 kcal/mol.

In the liquid state, if the same calculation is done with dispersive partial parameters of water[52] and with its vaporisation heat, $\Delta_{vap}H$, the hydrogen bonding contribution would be of -9.4 kcal/mol at 25°C.

As for the hydrogen bonding contribution, by comparing the value -12.17 kcal/mol (adsorption on solid) with that -9.4 kcal/mol (cohesion in liquid, considered as twofold hydrogen bond), we cannot refute the hypothesis about the twofold bindings of water on the surface of Avicel PH 101^R. This assumption is not in contradiction with that of Hollenbeck[40]. The same assumption is also valid for Fractosils.

4. Variation of isosteric enthalpy, $\Delta_{ads}H_{isost}$, isosteric entropy, $\Delta_{ads}S_{isost}$, and isosteric free enthalpy, $\Delta_{ads}G_{isost}$, of adsorption as a function of the degree of coverage, θ.

According to Stanley-Wood[45], Zografi[43-44], Hollenbeck[42], the integral heats of adsorption do not give a general sight into the variation of thermodynamic states of adsorbed water as function of the number of moles. Therefore, the isosteric quantities (calulated with equations 21, 22, 23, for a amount, n_a, of adsorbed water at different temperatures) are more suited to such a reprentation, and instead of

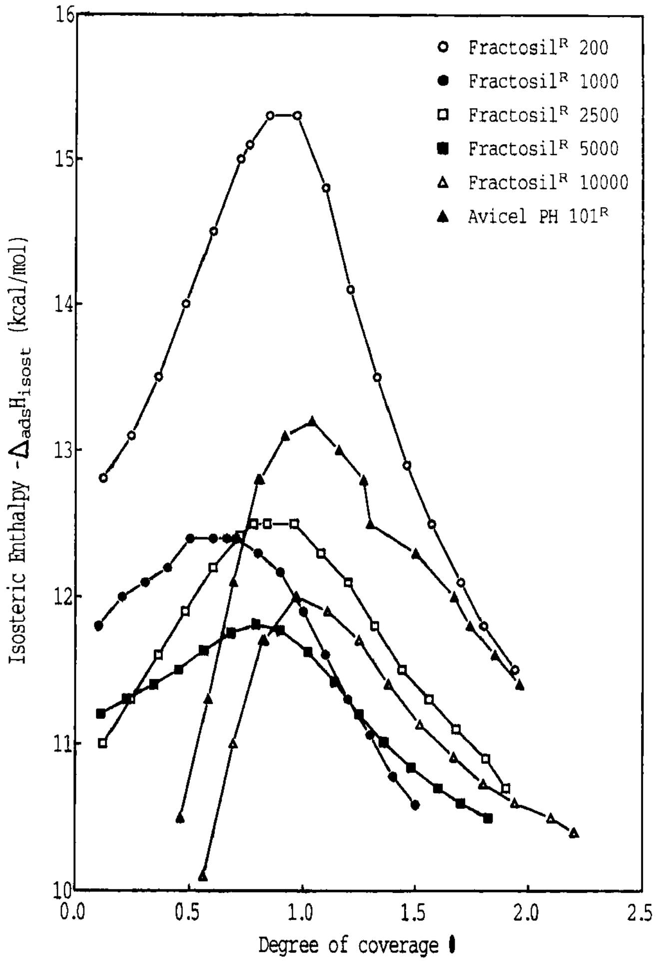

FIGURE 9

Variation of isosteric enthalpy, $\Delta_{ads}H_{isost}$, of adsorption for different solids as a function of the degree of coverage, θ.

the number of moles of adsorbed water, the degree of coverage or number of layer, θ, is used . To determine , θ, the knowledge of the amount of adsorbed water at monolayer, r_m, is required. As r_m varies with temperature (TABLE 3); the arithmetical mean of r_m for four temperatures is selected to compute the degree of coverage.

FIGURES 9, 10, 11 represent the variations of the isosteric thermadynamic quantities as a function of the degree of coverage.

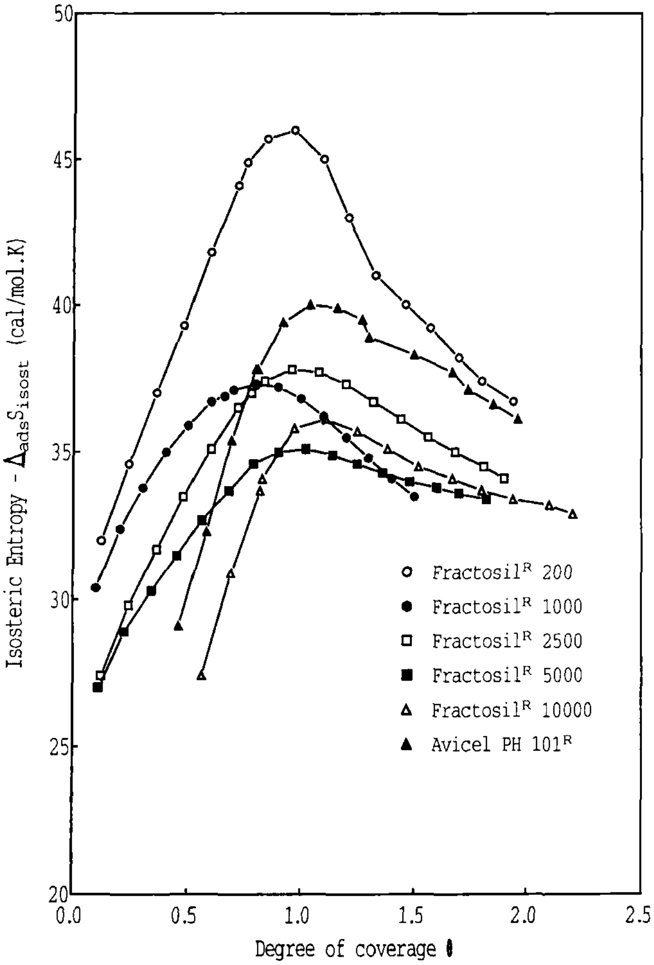

FIGURE 10

Variation of isosteric entropy, $\Delta_{ads}S_{isost}$, of adsorption for different solids as a function of the degree of coverage, θ.

Before the monolayer, the value of, $-\Delta_{ads}H_{isost}$, $-\Delta_{ads}S_{isost}$, increases with the degree of coverage, θ. At this stage, the energy of adsorption comes from two types of interaction: interactions between water and solid, and lateral interactions between molecules of adsorbed water. The variation of $-\Delta_{ads}S_{isost}$ corresponds to the transition from a relatively desordered state (free rotation) at the beginning of adsorption to a very ordered state at the monolayer.

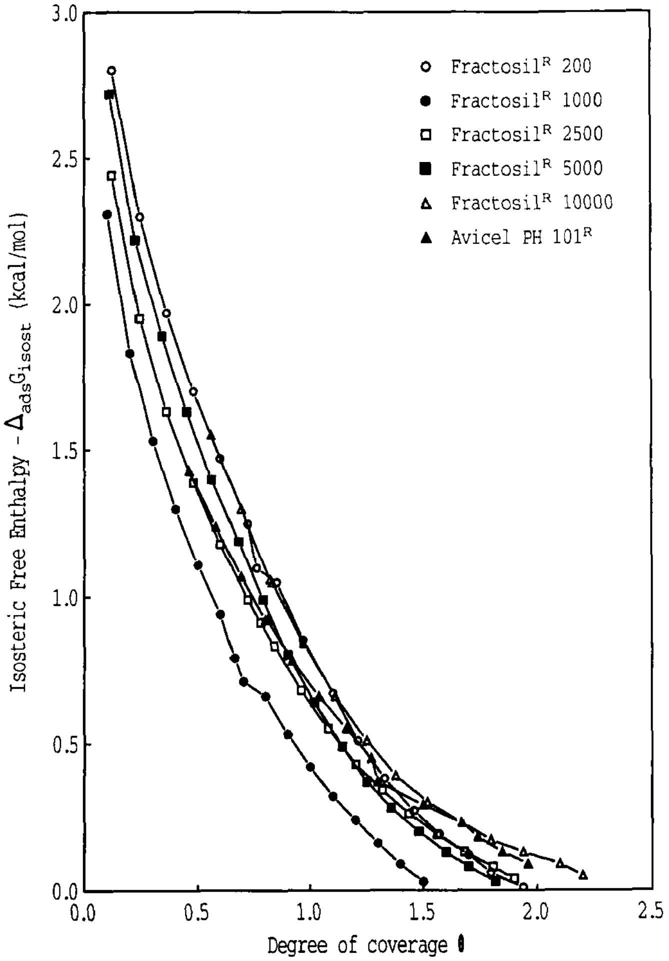

FIGURE 11

Variation of isosteric free enthalpy, $\Delta_{ads}G_{isost}$, of adsorption for different solids as a function of the degree of coverage, Θ.

At the monolayer, the values of, $-\Delta_{ads}H_{isost}$, and, $-\Delta_{ads}S_{isost}$, reach a maximun, and water molecules are strongly bonded.

Beyond the monolayer, the influence of the potential field of the surface falls strongly, and the effect of condensation is progressively felt. The double effects of the mentionned phenomena leads to the lowering of the energy balance sheet and the increase of the disorder.

Beyond the second layer, the process of condensation effectively starts, this is the reason why the value of, $\Delta_{ads}H_{isost}$, tends to be of $\Delta_L H = -10.05$ kcal/mol and that of $\Delta_{ads}S_{isost}$ will be -32.1 cal/mol K, entropy of the condensation at 313 K; the water is then in the free state. According to values of, K, (TABLE 5) and computed isosteric heats, the number of layers at saturation was approximated to 3.

As for free isosteric enthalpy, $\Delta_{ads}G_{isost}$, it decraeses steadily and tends to zero by the end of second layer (except for Fractosil 1000). The above results confirm Zografi's conclusions[44] for Avicel PH 101^R: Up to 4% of adsorption, water is strongly bonded, between 4% - 8% it is not completly free, and beyond 8% it is free (condensed water). This respectively corresponds to our three cases: ($\theta = 1$, $\theta = 2$, $\theta > 2$).

CONCLUSION

According to the results obtained, the possible conclusions are as follows:

1. Our proposed sample conditioning device is functional and reliable.
2. Frontal gas chromatography is easy to operate, and in the case of adorption of water, is a fast, reproducible and sensitive technique, indicated in particular for low relative humidities.
3. For data treatment of isotherms of water, the G. A. B. and the Hailwood-Horrobin models can both be used indiscriminately.
4. The amount of adsorbed water at the monolayer depends on the model used, the nature of solids and the working temperature.
5. For the set of Fractosils used, the working temperature has very little effect on the amount of water adsorbed. This is not the case with the Avicel PH 101^R.
6. As the values of Z showed, adsorption on Fractosil 5000 and 10000 is identified as mobile, whilst it is localized in the others.

7. In all cases studied, the isosteric adsorption enthalpy and entropy have a minimum at about the monolayer.

8. The net heat of adsorption at the monolayer depends on the nature of solids (values of C_B, C_G and β); however, that at intermediate layers is nearly the same for all solids studied (values of K and α).

8. The number of adsorbed layers was estimated at about 3 in this study.

9. A appropriate value of the constant, D, must be chosen to compute the net heats of adsorption, if G.A.B.'s model is used.

10. There are three thermodynamical types of adsorbed water: strongly bonded, weakly bonded and free (water condensed).

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