

ADSORPTION PHENOMENA ON GLASS SURFACES. III. A MICROCALORIMETRIC STUDY OF ADSORPTION OF *n*-BUTANOL ON HEAT TREATED SURFACES OF CONTROLLED PORE GLASS

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ABSTRACT

Flow microcalorimetry was used to study the adsorption of butanol on controlled pore glass (CPG) surfaces. Heats of adsorption and some thermodynamic data are reported for the adsorption process at the original, hydroxylated and hydrated surfaces and for those heat treated at temperatures of 450, 650 and 900°C. It was found that the molar free energy of adsorption is the same, 17 kJ mole⁻¹ for all the surfaces studied. The molar enthalpy and entropy of adsorption are indicative of steric effects caused by water molecules. For surfaces heat treated to 650°C monolayer coverage of butanol is close to 5 molecules per nm², the same figure as reported for the total number of vicinal and isolated silanol groups on the surface of silica.

INTRODUCTION

The paper describes microcalorimetric experiments of adsorption of *n*-butanol, a small monofunctional organic molecule, and thus a suitable probe, on the surface of controlled pore glass (CPG). The glass was pretreated by heating to various temperatures between 450 and 900°C to study the effects of the removal of surface hydroxyls [1,2]. In preceding papers the same was studied as a model for the adsorption of small monofunctional organic molecules at its hydroxylated surface [3,4] and the observed phenomena were related to the energetics of adsorption sites at the glass surface, to the structure of this surface, and to the calculated thermodynamic adsorption quantities.

The CPG's serve a variety of needs, some of which are related to laboratory techniques some to applied processes of column separation of various substances of biogenic origin (proteins, enzymes, viruses, biopolymers, etc.) [5–9]. They are also used as column fillers in gas and liquid chromatography techniques [10,11]. Since they are available in well defined bulk composition [12] with accurately controlled pore sizes and exhibit comparatively large specific surface areas, they can be

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proficiently used in a variety of experimental techniques, most notably in calorimetric studies of adsorption. It has been shown that heating the glass material to temperatures above 600°C results in the reduction of the number of available adsorption sites at the surface of CPG (as in any other silica based glass) and thus the extent of adsorption and its energetics are substantially altered.

It has been shown [3,4] that the adsorption phenomena at the glass/liquid interface are highly adsorbent-adsorbate pair specific. In accordance with this finding it was decided that *n*-butanol, a widely studied and convenient monofunctional organic molecule, showing good solubility in the carrier hexane and strong adsorption on the glass surface, would serve best as a molecular probe into the surface of CPG if studied by microcalorimetry.

EXPERIMENTAL

Apparatus

Microcalorimetric measurements were made using a commercially available microcalorimeter (Microscal Ltd., London). It was a flow microcalorimeter [13,14] featuring a two-piece standard sample cell with two pairs of matched thermistors in a bridge arrangement as detector. The sample volume (0.2 cm³) accommodated the coarse grained material under investigation on a suitable platinum screen support. A calibrated heating coil, imbedded into the cell, served for calibration purposes. Basic sensitivity was approximately $\pm 20 \mu\text{J}$. Flow rates of the carrier liquid and of the adsorbate solution could be adjusted over comparatively broad ranges. However, for the present experiments a flow of 3.3 cm³ h⁻¹ was found the most suitable [3]. This choice depended on the packing density of the sample column, and on the rate of the heat evolving process which in our case of adsorption from a non-aqueous solution was comparatively slow. This simple arrangement was used to measure the enthalpies of adsorption.

The amount adsorbed was determined using a precolumn of similar volume as the microcalorimeter cell filled with the sample material. The liquid flow from it was directly coupled to the microcalorimeter cell, the latter being used only as a retention time detector. The adsorbate solution was first introduced into the precolumn, where it adsorbed, and then at breakthrough penetrated the microcalorimeter cell and was recorded by the heat-of-adsorption peak.

Methodology of measurement

Two series of measurements were done with each sample. In the first series of experiments the heats (enthalpies) of adsorption were measured. The assumption involved in these experiments is that the solvent molecules at the glass surface are continuously displaced by the solute/adsorbate at a rate proportional to the concentration of the solute in the solution, until a dynamic equilibrium is reached.

This assumption being valid, a modified Langmuir type equation was used [3,14,15]

$$N/X = 1/(K_e - 1) X_m + (1/X_m)N \quad (1)$$

where N is the mole fraction of the adsorbate in the solution used, X is the adsorbed amount and X_m is the amount at the (statistical) monolayer coverage. K_e denotes an equilibrium distribution constant, which in all the cases studied is much greater than unity.

Correspondingly, and assuming that the adsorption process is accompanied by a change in enthalpy, a similar equation relates the concentration and the heat of adsorption

$$N/H = 1/(K'_e - 1) H_m + (1/H_m) N \quad (2)$$

where the constant K'_e includes a proportionality factor and is not necessarily numerically the same as in eqn. (1). H is the integral enthalpy of adsorption at N .

From the slope and the intercept of the straight line of N/H vs. N , the monolayer integral heat H_m was obtained, as shown in Fig. 1.

From the K_e of eqn. (1), the free energy of adsorption was obtained using

$$-\Delta G = RT \ln K_e \quad (3)$$

The standard entropy of adsorption was obtained using

$$RT \ln K_e = T \Delta S + H_m/X_m \quad (4)$$

The adsorbed amount was determined in the precolumn experiments from the

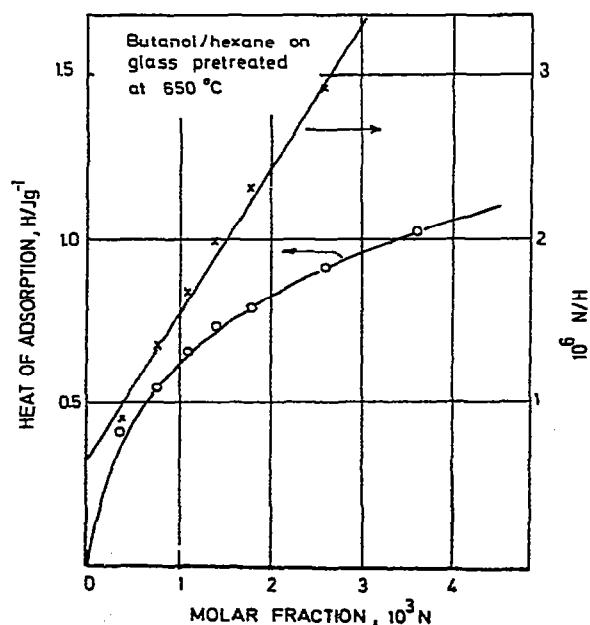


Fig. 1. The heat-of-adsorption (O) for the adsorption of butanol from hexane at 25°C on the surface of CPG vs. the molar fraction of the adsorbate in the carrier liquid. The straight line (X) is the linearized form of the adsorption isotherm, eqn. (2).

retention time, a procedure well known and much used in column chromatography [11]. In determining the t_0 , the zero-time correction, an experiment was made with the precolumn filled with a non-adsorbing medium but with similar characteristics of permeability. In this case it was crushed non-porous, borosilicate glass of a considerably lower specific surface area than the CPG used ($0.05 \text{ m}^2 \text{ g}^{-1}$ vs. $6.5 \text{ m}^2 \text{ g}^{-1}$), but of the same grain size (60–100 mesh). The t_0 time was determined from the recorder trace from the start of the liquid flow to the foot of the adsorption peak. One was making sure that the response time of the instrument was negligible for the actual range of measurements, or a correction was made for the same. The foot-of-peak reference point was preferred over the peak half-width procedure, since peaks differed widely in shape and size.

The adsorption time was determined in the same manner with identical samples of the CPG in the precolumn and the microcalorimeter cell. The retention time, $\tau = t - t_0$ is related to the adsorbed amount by

$$X = \tau FC / W \quad (5)$$

where F is the flow rate, C is concentration of the adsorbate in the solution in weight per volume units (the concentrations used were invariably low, see figures), and W is the mass of the sample in the precolumn.

It should be emphasized that in the sequence of experiments for each new concentration of the adsorbate in the flow solution a new sample of glass was inserted into the precolumn cell when measuring the adsorbed amount. For the heat of adsorption measurements in the microcalorimeter cell the same portion of the sample was used in the sequence of increasing concentrations of the adsorbate in the carrier liquid.

Materials

The controlled pore glass (CPG) was supplied by the Inorganic Glass Section of the National Bureau of Standards, Washington D.C., USA. It was a leached borosilicate glass, ground and sieved. The 60–100 mesh fraction was used in these experiments. The glass was characterized by a large specific surface area ($6.5 \text{ m}^2 \text{ g}^{-1}$, BET, argon), an average pore size of 225 nm (by mercury intrusion), and a bulk composition with near 2% of B_2O_3 [12].

Thermal treatment

A weighed sample of glass was placed into a silica glass ampoule and sealed to a high vacuum line. The heating was done in small cylindrical furnaces, controlling the temperature with NiCr/Ni thermocouples placed outside the ampoule but touching the silica glass wall of it. After some predetermined time the silica ampoule, still at an elevated temperature was sealed off the high vacuum line and cooled down. Submerged into the dry carrier hexane the ampoule was carefully broken. Hexane invaded the CPG without its surface ever becoming exposed to ambient air

TABLE I

Integral monolayer heats of adsorption of butanol at 298 K on original, thermally treated, and siliconized surfaces of controlled pore glass

State of the surface	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	H_m	
		(J g^{-1})	($\mu\text{J cm}^{-2}$)
Original	6.51	1.29	19.8
Thermally treated at			
$T=450^\circ\text{C}$	6.49	1.25	19.3
$T=650^\circ\text{C}$	6.52	1.25	19.2
$T=900^\circ\text{C}$, 5 h	4.20 ^a	1.17	27.8
$T=900^\circ\text{C}$, 20 h	1.10 ^a	0.30	26.5
Siliconized ^b	6.60	0.26	3.9

^a High variability: slow sintering influences surface area.

^b Siliconized surface: immersed into 3% solution of heavy silicone oil in CCl_4 , rinsed, dried at 150°C . See ref. 3 for details.

and moisture. As mentioned before, for each concentration of the adsorbate, and for each new measurement, a separate portion of CPG was prepared in the way described.

For each sample treated at a predetermined temperature a portion was used for specific surface area determination (argon, BET). The data are listed in the first column of Table I. In all the calculations the value of the specific surface area actually measured was used.

Chemicals

The carrier liquid for the flow-microcalorimetric experiments was *n*-hexane of chromatographic purity grade (Merck, Darmstadt). Standard *n*-hexane was prepared by drying with an activated Linde 5A molecular sieve, decanting and distilling, discarding the first 10% and the last 20% of the distillate. Any new batch of commercial, chromatographic grade *n*-hexane was tested against the "standard". If the heat of interaction with a portion of CPG in the same microcalorimetric cell under standard conditions did not exceed 0.2 mJ (that is 10 times the ultimate sensitivity of the microcalorimeter used) it was considered satisfactory and the hexane was used without further purification.

The adsorbate, *n*-butanol, was a commercially available chromatographic purity grade chemical (Fluka, Buchs). Solutions were prepared thereof in *n*-hexane of 0.02 to 0.2 w/v%, that is up to a molar fraction of 5×10^{-3} .

RESULTS

From measurements of adsorption isotherms on various samples of CPG, pre-treated at different temperatures, and from calculations, involving the linearized

adsorption isotherms shown in Fig. 1, the integral monolayer heats (enthalpies) of adsorption were obtained. The results are shown in Table I, along with the specific surface areas measured for each sample. The heats of adsorption are not much changed by thermal treatments from the original glass surface up to and including a short (5 h maximum) heating at 900°C. After prolonged heating at this temperature a significant decrease in the values was observed, approaching those for siliconized surfaces. If the values were recalculated for unit surface area, the H_m values indicated an increase for the 900°C treatment. Also, the departure is characteristic of those values obtained from the values measured on siliconized surfaces. It seems that a mechanism of adsorption is activated which is not operative at surfaces never subjected to this high temperature. One should note that above 900°C, fast sintering was observed, resulting in pore closure and characterized by a significant decrease in the specific surface area. Thus, 900°C is the highest temperature for this type of experiment with CPGs.

In Fig. 2 the measured adsorption isotherms are shown for the same CPG sample. The isotherms are shifted towards lower heats of adsorption with increasing temperatures of pretreatment. The recalculation of the isotherms into heats of adsorption per unit surface area are shown in Fig. 3. While the three isotherms, for the untreated surface and for the two lower temperatures tend to be indistinguishable one from another within the expected experimental error, there is some departure for both the 900°C isotherms. The one for shorter heating times (5 h) shows higher heats of adsorption than any other, the one for longer (20 h) tends to lower heat values. However, the monolayer values of the heat of adsorption are still considerably

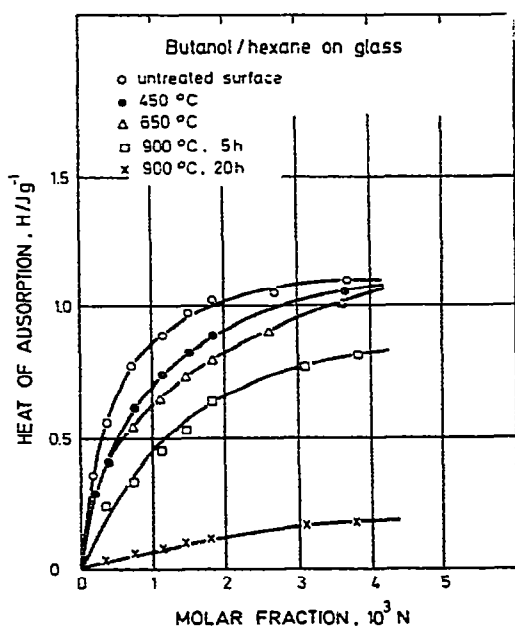


Fig. 2. The 25°C adsorption isotherms (heats per unit mass vs. molar fraction of adsorbate) for the adsorption of butanol on CPG for original and for heat treated 450, 650 and 900°C (5 and 20 h) surfaces.

higher, as shown in Table 1. Because of the large error involved in measuring and calculating the data for the 900°C treated CPG, no further experiments and calculations were attempted for these samples. For the untreated surface of CPG and for the samples heated to 450 and 650°C the adsorbed amounts were measured and the values were calculated for the monolayer coverage, thus enabling some estimates of basic thermodynamic quantities. The results are shown in Table 2. The values for the free energy of adsorption of butanol of the various surfaces of CPG seem to be the same to within experimental error. The enthalpies of adsorption for the thermally treated surfaces are however significantly different from the original one, although still considerably higher than those for the siliconized surface. Thus, a significant entropy term is appearing on the basis of these measurements and such calculations.

In order to clarify the nature of adsorption in these three cases, the original surface and that treated at 450 and 650°C, calculations were made from the adsorption isotherms on the molar heats of adsorption vs. coverage of the surface by butanol. Equilibrium conditions were assumed for each concentration of the adsorbate in the carrier liquid. The isotherms are shown in Fig. 4. The original surface of CPG seems to be highly heteroenergetic as shown by a steep decrease in the molar heats with coverage. Thermal treatment tends to remove the most energetic adsorption sites, and the surface appears almost monoenergetic.

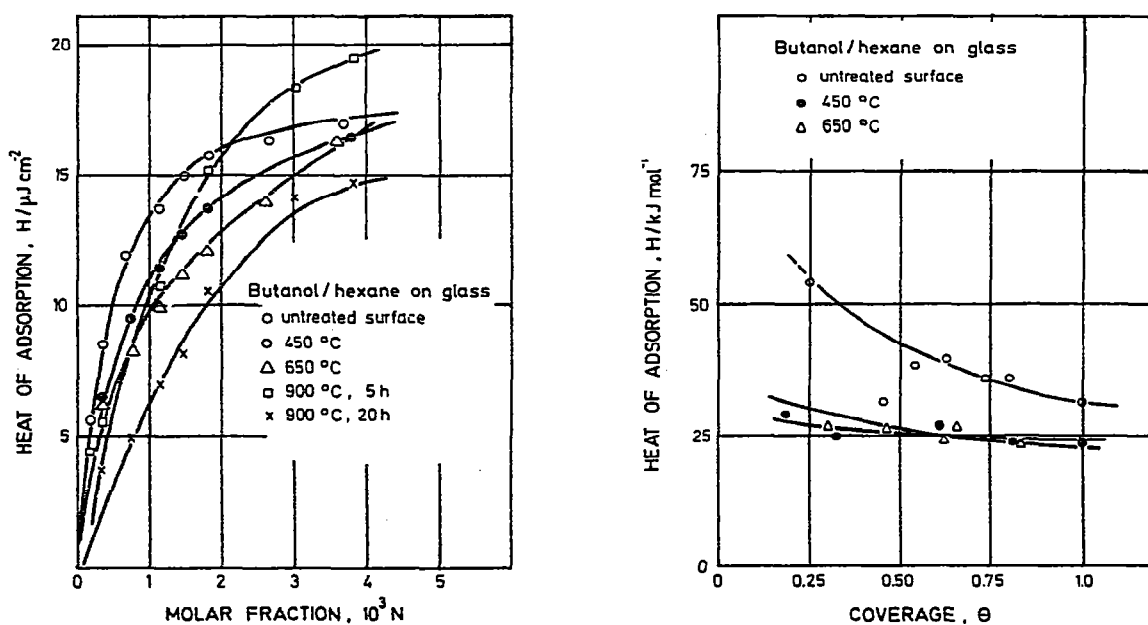


Fig. 3. The 25°C adsorption isotherms (heats per unit surface area vs. molar fraction of adsorbate) for the adsorption of butanol on CPG for surfaces as in Fig. 2.

Fig. 4. Integral molar heats of adsorption of butanol at 25°C on CPG vs. surface coverage of adsorbate for the original and heat treated surface.

TABLE 2

Thermodynamic parameters for the adsorption of butanol at 298 K on original, thermally treated and silicized surfaces of controlled pore glass

State of the surface	H_m ($J g^{-1}$)	X_m (10^5 mole g^{-1})	$\ln K_c$	$-\Delta G$ (kJ mole $^{-1}$)	$-\Delta H$ (kJ mole $^{-1}$)	ΔS (J mole $^{-1} K^{-1}$)
Original	1.29	4.10	6.985	17.3	31.5	-48
Thermally treated at						
$T=450^\circ C$	1.25	5.44	6.891	17.1	23.0	-20
$T=650^\circ C$	1.25	5.28	6.867	17.0	23.7	-23
Silicized ^a	0.26	1.64	6.510	16.1	15.8	(+1) ^b

^a For treatment see footnote Table 1.^b Uncertain value, difference of two large, close values.

DISCUSSION

The results presented indicate two characteristic features for the adsorption processes on heat treated surfaces of glass. Firstly, the molar free energy of adsorption of butanol is the same (within the precision of the experiment) for the original and for the heat treated surface, and for that matter also for the siliconized surface of CPG. The molar enthalpies of adsorption are different, leaving a significant entropy term to account for the mechanism of adsorption. Apparently the basic adsorption site is the silanol group, as has been shown to be true for the adsorption of hydrocarbons [16,17] and for the interaction in surface derivatization with 3-methylchlorosilane [18], hexamethylsilazane [19], and for many cases involving water and other adsorbates [18–27] on silica surfaces.

Secondly, the adsorption is less sterically hindered in the absence of adsorbed water and possibly of the geminal (or vicinal) silanol groups. These have been shown to be removed from the surface at temperatures in excess of 600°C. Furthermore, the boronol groups, strong adsorption sites for the adsorption of electro-donating molecules (ammonia, amines), were not preferential adsorption sites for butanol.

Uesugi et al. [1] have shown that heat treating the CPG's results in energetically more homogeneous surfaces for the adsorption of aliphatic and aromatic hydrocarbons. Hydrocarbons were shown to adsorb also on top of silanol groups, as is the case for a functional group molecule like butanol. The observed decrease in the integral molar heat of adsorption with coverage for the original surface (Fig. 4) and the decrease of the molar entropy of adsorption by heat treatment and by surface blocking by siliconization [3] (Table 2), leads to the conclusion that the changes induced are mostly eliminating steric hindrance to butanol adsorption. Once the adsorbed water molecules are removed from the surface, the butanol adsorbate "sees" only the silanol adsorption sites. The number of these remains the same as indicated by the monolayer values for the 450 and 650°C treated CPG. In both these glass surfaces butanol adsorbs to form a monolayer of 5.0 and 4.9 molecules per nm². These figures coincide significantly with the often quoted figure of 4.6 nm⁻² [28,29] for the total numbers of OH groups on the silica surface. Thus, it seems, that after the heat treatment to 650°C, the number of geminal and vicinal silanol groups remains the same. An alternative interpretation would be a fast rehydroxylation of the siloxane groups, either by residual water in the liquid (which is not probable considering the experimental techniques), or by fast derivatization by butanol. The observed reversibility of adsorption contradicts this assumption. Also, the heats of adsorption involving rehydroxylation of the siloxane groups would have to be much higher, somewhere in the range of the dissociation energies of interacting surface hydroxyls. These as measured by IR techniques [25] amount to some 500 kJ mole⁻¹. Armistead et al. [29] has shown that for silica surfaces single surface silanols remain intact for all the temperatures up to 600 ± 50°C, but that the vicinal and geminal groups are progressively removed. This seems to contradict the observations reported here for glass surfaces.

In order to clarify the state of the surface after heat treatment of 650°C, spin

label techniques were used [30]. The original and the heat treated surfaces were labelled with a spin label with a hydroxyl functional group: 2,2,6,6-tetramethyl-4-hydroxy piperidine-1-oxyl, a molecule with a cross sectional area in adsorption of 0.6 to 0.8 nm². In both cases the same density of spin labels per unit surface was observed in the ESR spectra. This supports the finding of microcalorimetric measurements that the total number of available adsorption sites did not alter during the heat treatment up to 650°C, or, rehydroxylation occurred immediately after exposure of the heated sample to the liquid.

With the present level of experimental information it remains as a conclusion that heat treatment produces homoenergetic adsorption sites of a concentration of 5 nm⁻². Thus a practical result is available for the application of CPG, where energetically homogeneous surfaces are essential. A further improvement in the information level would be found in using experiments of surface derivatization as a chemical tool of investigation of the distribution of adsorption sites in CPG, and in experiments with smaller spin-labels, if such convenient molecules could be made available.

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