

# Surface charge and adsorption of sodium ions at the controlled porosity glasses/electrolyte interface

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Controlled porosity glasses (CPGs) are used as adsorbents, supports or catalysts. Their properties depend on the amount of surface boron and sodium concentration. The surface boron and sodium concentration can be changed by proper thermal treatment. The presented paper deals with the change of charge surface density and pH of point zero charge of the thermally treated CPG. The surface reaction constants according to the site binding theory of the electric double layer were calculated on the basis of the surface charge data. The results of  $\text{Na}^+$  adsorption on the CPGs are presented.

## 1. Introduction

The silica gels are most often used as chromatography column filling and/or supports for chromatography sorbents preparation. Nevertheless, controlled porosity glasses (CPGs) may also be employed due to the possibility of obtaining controlled-porosity structures of relatively great thermal and solvolytic resistance [1–3].

The starting materials applied to prepare CPGs belong to a group of three component alkali–borosilica glasses of the Vycor type [4]. During the successive stages of CPG production (heating of the starting material in order to separate the two phases – silica and alkali–borate – and the leaching of the latter) a siliceous skeleton is formed containing a small amount of boron (up to 6%  $\text{B}_2\text{O}_3$ ) and alkaline oxide (up to 0.5% of mostly  $\text{Na}_2\text{O}$ ) [4, 5]. The experimental investigations showed that, owing to the secondary heating of porous glass in the temperature range 673–1073 K, there existed the possibility of CPG surface enrichment in sodium and boron atoms [6–8]. Under the conditions mentioned above, sodium and boron atoms remaining after preparation in the formed siliceous skeleton diffuse to the surface. A very long period of heating at higher temperature leads even to the appearance of  $x\text{Na}_2\text{O} \cdot y\text{B}_2\text{O}_3$  clusters [8].

The acid–base properties of the hydroxyl groups at the CPG siliceous surface depend on the amount of sodium and boron on the surface [9, 10]. The character of the hydroxyl groups affects the formation of a surface charge at the CPG/electrolyte interface owing to the adsorption of  $\text{H}^+$  and background electrolyte ions.

The aim of this work was to investigate the influence of the thermal treatment on the acid–base properties of the surface hydroxyl groups. The surface charge at the CPG/electrolyte solution was measured

using the potentiometric titration technique. The adsorption of sodium and chloride ions on the surface of CPGs were also observed.

## 2. Experimental procedure

### 2.1. Materials

The initial glass of controlled porosity was obtained from a Vycor-type glass composed of 7 mol %  $\text{Na}_2\text{O}$ , 23 mol %  $\text{B}_2\text{O}_3$  and 70 mol %  $\text{SiO}_2$ .

In order to transform this crude material into porous sorbents (glass 0), a 102–150  $\mu\text{m}$  fraction of the Vycor glass was heated at 833 K for 4 h and then leached following the previously described procedure [5, 11].

For various enrichments of the glass surface in sodium and boron atoms, the separate samples of the obtained porous glass 0 were heated at 973 K for 1, 3, 6, 13, and 21 h (glasses 1NW, 3NW, 13NW, 21NW, respectively, where NW indicates unwashed).

The prepared materials were next washed (using redistilled water, 1.5  $\mu\text{S}$ ) to the constant level of the specific conductivity of the water. In this way the materials: 1W, 3W, 6W, 13W and 21W were obtained (W indicates washed).

### 2.2. Methods

The surface charges of the prepared initial CPG and thermally enriched CPGs with unwashed and washed surfaces were estimated using the method of the potentiometric titration of suspension. pH measurements were carried out employing a pH-meter PHM-84 and a recorder REC-61 Radiometer (Copenhagen, Denmark). As an indicator electrode, a glass electrode G 202C was applied and, as a reference electrode, a calomel electrode K 701 was used. The

measurements of ion adsorption from electrolytes were made using the radiotracer technique. The loss of ions from the solutions was observed. Na-22 or Cl-36 were used in order to label the electrolyte solutions.

### 3. Results and discussion

Fig. 1 presents the relationship between the hydrogen-ion concentration adsorbed on the unwashed and washed, thermally treated glasses and the pH in 0.001 M NaCl solution. For clarity of presentation, Fig. 1 contains only the curves for two pairs of glasses.

As is apparent from Fig. 1, the largest consumption of  $H^+$  ions is observed in the case of unwashed materials. It must be stressed that the consumption difference increases with an increase of the thermal treatment time. The higher  $H^+$  adsorption is connected with the neutralization of  $xNa_2O \cdot yB_2O_3$  compounds formed on the controlled porosity glass surface after its additional thermal treatment. Assuming that the difference between plots corresponding to unwashed and washed glasses results mainly from  $Na_2O$ , the amount of sodium oxide leaving the surface during washing process can be estimated. The  $Na_2O$  amounts washed out from variously heated CPGs calculated on the basis of the potentiometric titration curves and spectrophotometric data are included in Table I. There is no doubt that the data obtained by means of the spectrophotometric method are more precise. The potentiometric results confirm the responsibility of sodium ions for the elevated consumption of hydrogen ions in the case of unwashed, thermally treated porous glasses.

Surface charge density as a function of pH for the washed samples of heated porous glasses measured in 0.1 M NaCl solution is presented in Fig. 2a and b. The obtained results (see Fig. 2a and b) confirm the earlier observed relationship between the point zero of charge (pH pzc) and heating time [10]. The increase of the thermal treatment leads to surface enrichment in boron atoms. In consequence, an increase in the positive charge surface concentration is observed.

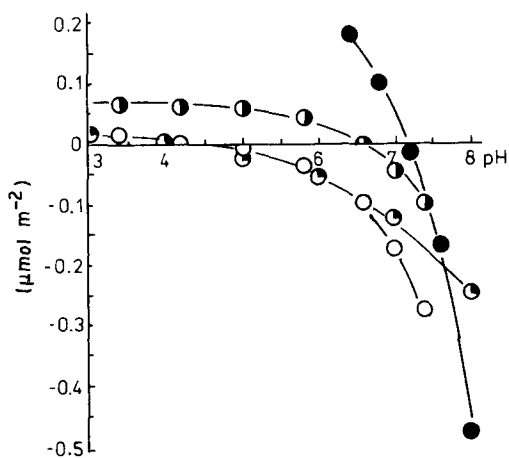
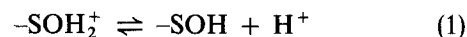


Figure 1 Consumption of  $H^+$  ions by (○) washed and (●) unwashed glass 0 and (○) washed and (●) unwashed CPG heated for 13 h.

Taking into account the relationship presented in Fig. 2 and the titration data for the lower ionic strength of the background electrolyte, the ionization and complexation constants of the hydroxyl groups were calculated, see Table II. These values were estimated assuming a constant surface concentration of hydroxyl groups for each investigated material (5.0 hydroxyl groups/nm<sup>2</sup>). As is apparent from Table II, the ionization constants connected with the following reaction



have changes of about four orders whereas the ionization constants corresponding to formation of the

TABLE I Sodium ions concentration at CPG surfaces

Heating time (h)	Concentration ( $\mu\text{mol m}^{-2}$ ) measured by	
	potentiometry	spectroscopy
0	0	0.046
1	0	0.098
3	0.1	0.169
6	0.15	0.202
13	0.31	0.197
21	0.29	0.213

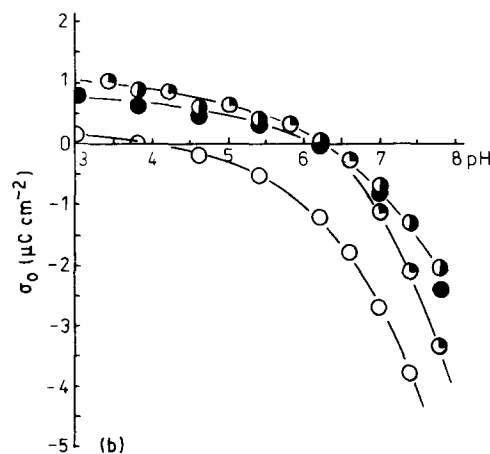
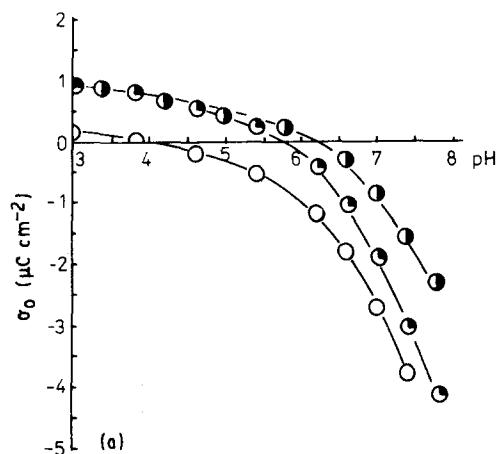


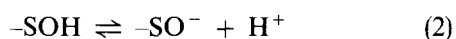
Figure 2 (a) Surface charge density at the CPG/0.1 M NaCl solution for samples: (○) 0W, (●) 1W, and (●) 3W. (b) Surface charge density at the CPG/0.1 M NaCl solution for samples: (○) 0W, (●) 6W, (●) 13W, and (●) 21W.

TABLE II Surface ionization and complexation constants for CPG calculated using Davis *et al.* method [12]

Heating time (h)	Constants <sup>a</sup>			
	pK <sub>a1</sub>	pK <sub>Cl<sup>-</sup></sub>	pK <sub>a2</sub>	pK <sub>Na<sup>+</sup></sub>
0	0.7	0.69	8.08	8.07
1	4.32	4.31	8.94	8.94
3	5.08	5.07	9.31	9.30
6	3.74	3.7	9.25	9.2
13	4.52	4.48	9.5	9.45
21	4.32	4.31	9.68	9.67

<sup>a</sup> pK<sub>a1</sub>, pK<sub>a2</sub> are effective surface ionization constants, pK<sub>Cl<sup>-</sup></sub> is the chloride surface complexation constants, pK<sub>Na<sup>+</sup></sub> is the sodium surface complexation constant.

negative charge (see Reaction 2, below) have changes of only about one and a half orders.



The latter results are in agreement with the observed shift of pH pzc in the direction of higher pH (see Fig. 2a and b). The presented data suggest that the greatest changes in the surface properties of the investigated material occur during the first 6 h heating (compare the results from Tables I and II and Fig. 2a and b). Thermal treatment for longer than 6 h causes relatively small changes of surface character. This does not mean that the boron diffusion process stops. According to the literature [6, 7], it is probably continued but with the boron collected in the form of surface boron clusters of almost constant surface area. Besides the reaction of the surface charge formation described above, the site binding theory predicts two other reactions in which electrolyte ions take part. According to the above theory, in the case of NaCl solution the following reactions could be considered



During the adsorption measurements of the electrolyte ions, the Cl<sup>-</sup> adsorption was not observed in any of the investigated samples.

The results of Na<sup>+</sup> adsorption on the CPG surface from NaCl solution (0.001 and 0.01 M) are shown in Figs 3 and 4. The obtained curves (Na<sup>+</sup> adsorption as a function of pH) are typical for cation adsorption on a soluble metal oxide surface. The diminution of Na<sup>+</sup> adsorption with pH increase can be explained as being a result of Reaction 3 and coulombic interactions with surface charge. However, the Na<sup>+</sup> adsorption changes a little with the thermal treatment time. As the surface reaction constants of Na<sup>+</sup> complexation change by about one and half orders and most of the adsorbed Na<sup>+</sup> ions should be involved in this reaction, the obtained values of Na<sup>+</sup> adsorption are difficult to explain in terms of this reaction. It can be assumed that, because of high sorbent porosity, the adsorbed sodium ions interact with the surface hydroxyl groups and among one another. In the porosity system, the interaction would be not only horizontal but also

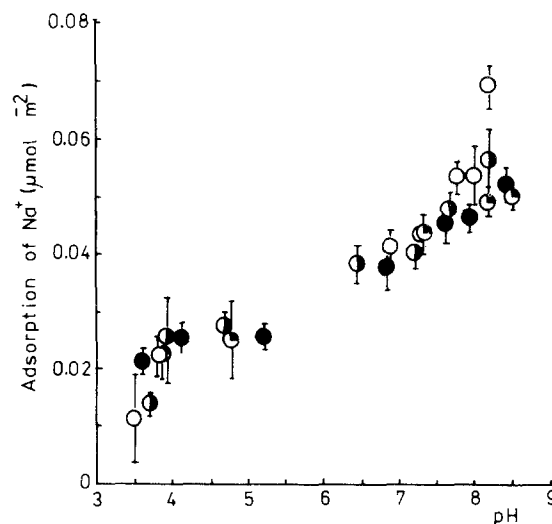


Figure 3 Adsorption density of Na<sup>+</sup> ions as a function of pH for CPG samples: (○) 0W, (◐) 6W, (◑) 13W, and (●) 21W, in 0.001 M NaCl.

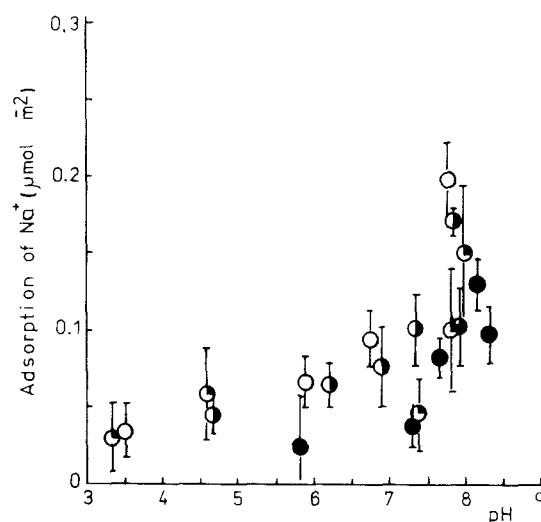


Figure 4 Adsorption density of Na<sup>+</sup> ions as a function of pH for CPG samples: (○) 0W, (◐) 1W, (◑) 13W, and (●) 21W, in 0.01 M NaCl.

vertical. Consequently, this can lead to a significant decrease in adsorption and lack of differences among the investigated samples.

#### 4. Conclusions

1. The presence of sodium ions in the CPG surface leads to an increase in hydrogen ion consumption.
2. Thermal treatment causes an increase in the concentration of positively charge surface groups and the shift of pH pzc to the alkaline range.
3. The surface reaction constants calculated on the basis of the titration data confirm the second conclusion. The constants corresponding to the reaction of positive group formation change by four orders, whereas the constants corresponding to the reaction of negative group formation change by one and a half orders.

4. Insignificant changes of sodium adsorption can be explained by relatively small changes of the surface complexation constants of sodium ions.

### Acknowledgement

This work was supported by Grant PR-I-08.

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*Received 2 February  
and accepted 30 November 1990*