Influence of surface modification of porous glasses on their surface free energy

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Investigations of zeta-potential changes of initial and thermally treated controlled-porosity glasses (CPGs), whose surfaces were covered with different amounts of n-octane and/or nitromethane, are presented. The dispersive (γ_s^d) and non-dispersive (γ_s^n) components of the surface free energy were then calculated using the relationships obtained. γ_s^d was found to be practically independent of the treatment time (a small increase in the range of 4 mJ m^{-2} can be seen), but a considerable decrease in γ_s^n was observed (from 76.95 to 27.2 4 mJ m^{-2}). In the case of CPG modified with γ-aminopropyltriethoxysilane an increased hydrophobic character of the surface was found. This was reflected in increased γ_s^d and decreased γ_s^n values.

1. Introduction

Surface free energy is one of the parameters which can be useful in controlling sorbent surface properties. The energy, expressed in a simplified way as a sum of dispersive and non-dispersive components, really results from various intermolecular interactions [1-3]. Knowledge about surface free energy (especially its components) can help one to choose a suitable solvent and its composition for various adsorption and chromatographic processes. The components can also be very useful to control different surface processes such as dehydroxylation, chemical modification, deposition of stationary phases and carbonization [4].

However, in the literature the data concerning the subject are rather scarce. Therefore, it seemed to us interesting, both from the practical and theoretical points of view, to determine the dispersive and non-dispersive components of the surface free energy of some sorbents.

Controlled-porosity glasses (CPGs) are chromatographic sorbents which possess a high chemical, thermal and mechanical resistance. They are also characterized by a very narrow pore size distribution in a wide range of mean pore diameters [5].

Glasses of controlled porosity are siliceous materials prepared by thermal treatment and a leaching process, as in glass of the Vycor type [6-8]. During heating (400-700 °C) the glass mixture from a certain region of the ternary system $R_2O-B_2O_3-SiO_2$ separates into two continuous phases: a silica phase not dissolved in acids, and an alkali-metal borate phase which can be removed from thermally treated Vycor glass by leaching in acids.

As a result of the preparation process a porous material composed of silicon dioxide (94-99%) (being the main component), B_2O_3 (1-6%) and Na_2O (0.03-0.5%) is formed [9]. As is known from the literature, CPGs are characterized by strong adsorp-

tion properties which are due to the presence of surface groups and boron atoms [10]. It has been proved that the surface boron concentration can easily be changed by heating a CPG in the temperature range 400-800 °C [9-12]. The processes occurring on the surface during the thermal treatment of the glasses also change the magnitude of the forces operating at the interface.

The properties of siliceous materials can also be changed by chemical modification. Usually this is realized by chemical reaction between hydroxyl groups existing on the surface of the modified support and an appropriate agent [5, 13]. Thermal and chemical modifications of siliceous materials are largely applied to reach defined adsorption and chromatographic properties.

This paper deals with the type and magnitude of interfacial interactions of unmodified and modified CPGs which are typical sorbents used in chromatography, biochemistry and biotechnology. The results presented are to be considered as a preliminary attempt at the above-mentioned verification of solvents for adsorption and chromatography processes.

2. Experimental procedures

2.1. Materials

2.1.1. CPG preparation procedure

The CPG was obtained from a Vycor-type glass composed of 6.0% Na_2O, 68.4% SiO_2 and 25.6% B_2O_3. In order to change the original material into a porous sorbent, a 150-200 μm fraction sample of Vycor glass was heated at 594 °C for 72 h, then leached in H_2SO_4 and KOH solutions according to the previously described procedure [6, 7]. As a result a CPG of pore diameter $D = 52$ nm and pore volume $V_p = 1.28$ cm^3 g^{-1} was obtained. The porous material

was next crushed and the fraction not sedimenting over 1 h (henceforth referred to as CPG I) was used for further investigations. To enrich the glass surface with boron atoms, individual portions of CPG I were then heated at 590 °C for 2, 20 and 120 h (termed further as glasses II, III and IV, respectively).

2.1.2. Chemical modification of CPG surface

5 g portions of glasses I–IV, placed in a glass flask, were mixed with 400 ml of a 20% solution of γ-aminopropyltriethoxysilane (APTES) prepared in dry toluene [13, 14]. The mixture was refluxed over 6 h. The product was then washed in dry toluene and next in ethanol until there was an absence of APTES in the supernatant, and finally dried overnight in an oven at 120 °C (CPG–APTES I and IV, respectively).

2.2. Methods

(i) The method described elsewhere [15–20], based on zeta-potential measurements in the system solid/organic liquid film–water, was applied for the determination of the CPG surface free energy components (dispersive γ_s^d, and non-dispersive γ_s^n). Samples were covered with a known amount of n-octane (for γ_s^d determinations) or nitromethane (for γ_s^n determinations) and zeta potentials were measured in triply-distilled water [15–20]. Then by graphic integration [15–20] of the experimentally obtained relationship between the film volume and zeta potential, the film pressure π was evaluated. Analysing the inflexions on the curve showing the relationship between the film pressure and the number of statistical monolayers of the film of n-octane or nitromethane, surface free energy components for the investigated materials were calculated.

Measurements of the electrokinetic potential were carried out by means of microelectrophoresis, employing a zetameter EKB 11 (Ekobudex, Gdańsk, Poland). The zetameter used consisted of a visual system (microscope, camera and monitor), microcomputer panel with a printer (controlling the experiment) and a rectangular quartz measuring cell with electrodes (Pt cathode and Mo anode). The experiments were carried out at a potential gradient of $10 \, V \, cm^{-1}$, using the parabola or White's methods [21]. The following procedure was employed during measurements: 0.05 g of the investigated material, placed in a glass ampoule, was cooled in liquid nitrogen. A proper amount of n-octane or nitromethane was injected by means of a microsyringe and then the outlet of the ampoule was quickly sealed in a flame. Next, the ampoule was heated at 100 °C for 2 h and shaken every 30 min. After sample cooling, a 50 ml suspension was prepared in triply-distilled water [19–20].

(ii) Specific surface areas (BET) were determined by the Nelsen–Eggertsen thermodesorption method [22], using nitrogen as adsorbate and laboratory-made equipment [23].

(iii) Mean pore diameters for the prepared materials were calculated from porosimetric data. Porosimetric measurements were carried out employing a mercury porosimeter, Type 2000 (Carlo Erba, Milano, Italy).

(iv) Amounts of bonded APTES radicals were calculated from thermogravimetric experiments. A derivatograph model Q 1500 (MOM, Hungary) was applied for this purpose.

3. Results and discussion

In Table I are collected the results for specific surface areas (S_{BET}) for thermally treated and chemically modified materials. The values presented indicate a decrease of S_{BET} with thermal treatment time and/or after chemical bonding by APTES radicals. According to the data reported previously [11, 12] thermal treatment causes diffusion of boron and sodium atoms from the bulk CPG phase toward its surface. During heating the surface enriches mainly in boron atoms. A suitably long thermal exposure may even cause formation of borate clusters on the porous glass surface [11, 24]. Simultaneously with this process, a partial dehydroxylation occurs on the heated CPG surface. As already discussed, changes in the specific surface area are due to changes in the chemical properties of the CPG surface taking place during thermal treatment. The same explanation is adequate for chemically modified samples. Of course, the changes in the surface chemical properties will also influence the surface free energy components.

Figs 1 and 2 show typical dependences of zeta potential (ζ) versus the film volume (v) of n-octane and nitromethane, respectively, for porous glasses I and IV. A similar shape of the ζ changes as that for glass I was observed for glasses II and III, but they are not presented in this paper. However, a gradual diminution of the extrema of the curves was observed in the direction from glass I to glass III. This can be explained as a result of the surface enrichment in boron

TABLE I Some physico-chemical properties of the CPGs investigated

Glass No.	Thermal treatment (h)	Specific surface area, S_{BET} (m² g⁻¹)		Coverage density by –CH₂CH₂CH₂NH₂ radicals (µmol m⁻²)
		Non-silanized	Silanized	
I	0	73.45	58.8	3.62
II	2	73.9		
III	20	62.4		
IV	120	55.0	52.61	3.27
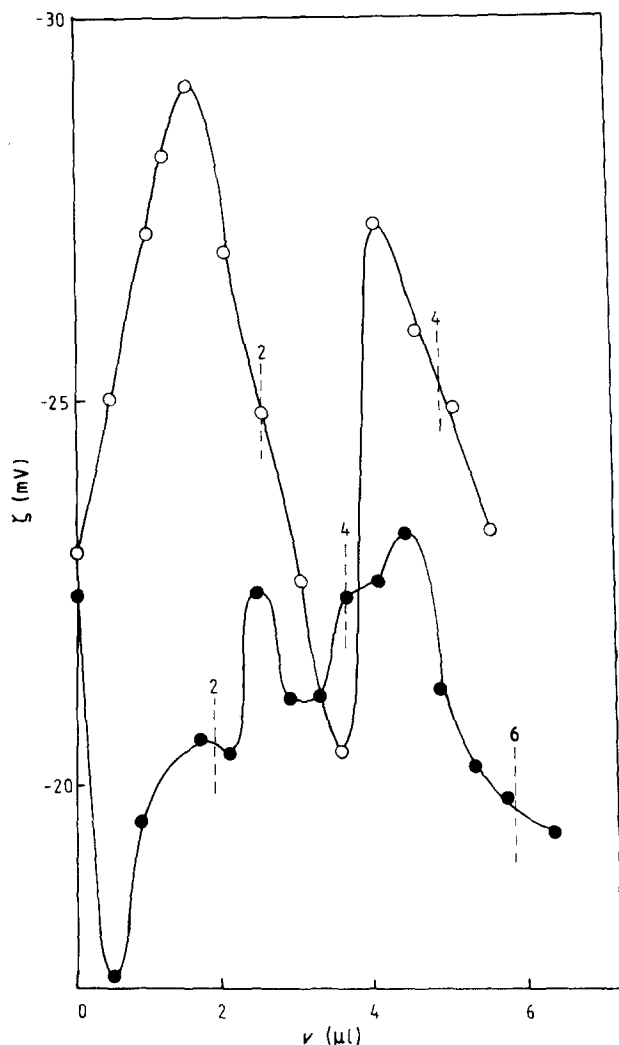
Figure 1 Zeta potential (ζ) of ($\bigcirc$) glass I and ($\bullet$) glass IV in water as a function of n-octane film volume (v). Dashed lines on the curves show the calculated monolayers.

Figure 2 The same relationships as in Fig. 1 for nitromethane: ($\triangle$) glass I, ($\blacktriangle$) glass IV.

atoms and partial dehydroxylation occurring especially at the beginning of CPG heating.

The different course of the zeta potential changes for glass IV (Figs 1 and 2) points to a significant difference in its properties in comparison with those of CPG I, II and III. Glass IV was obtained from glass I by prolonged (120 h) thermal treatment. According to previous work [9, 11, 12, 24–26] such a treatment causes maximal surface enrichment with sodium and boron atoms. These elements start to form borate clusters which become additional heterogenetic centres.

The vertical lines on the curves (Figs 1 and 2) denote the calculated monolayers of n-octane and nitromethane films, assuming for cross-sectional areas 0.4234 and 0.25 nm², respectively [27, 28]. From the observed dependences the film pressures of the liquids on the glass surface were determined.

Fig. 3 shows the relationship between the film pressure and the number of statistical monolayers of n-octane for glasses I and IV (curves I and IV, respectively). As can be seen, the curves are stepped with inflexions which, as in the case of some insoluble liquids on a water surface [29, 30], point to changes in the film structure. It was suggested previously [31, 32]
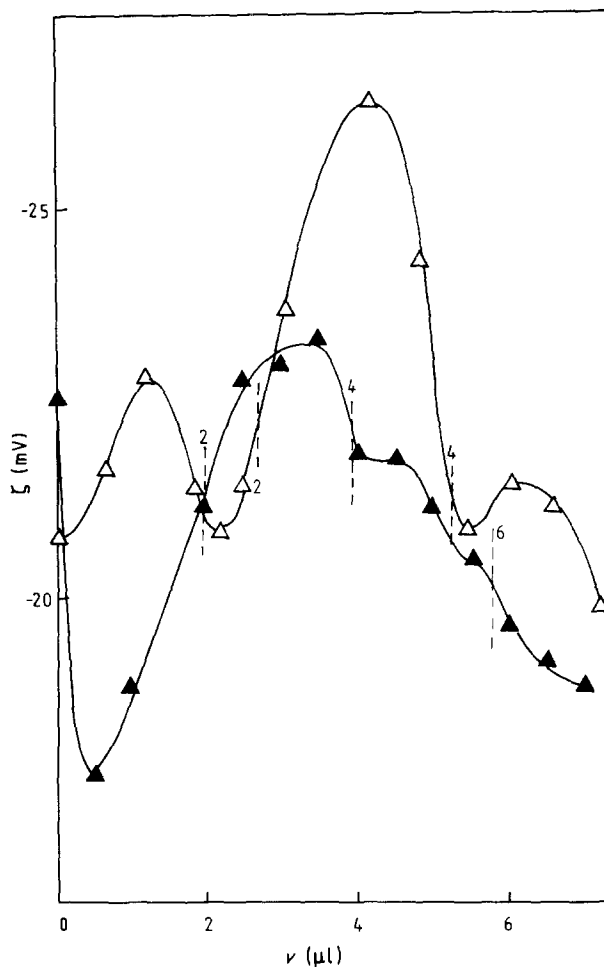

Figure 3 Film pressure π of n-octane for ($\bigcirc$) glass I and ($\bullet$) glass IV versus the number of statistical monolayers.

that some of the inflexions result from a "completion" of particular wetting processes like spreading, immersion or adhesion when considered in terms of the film thickness. For the tested samples of porous glasses wetted by n-octane (Fig. 3), the work of spreading wetting has been considered to be equal to the film

pressure at the inflexion points lying at ca. 3 and 4 monolayers, respectively. Based on these values, the dispersive component (γ_s^d) of the surface free energy was calculated from the following equation [16–20, 33]:

$$\pi_s = W_s = -2\gamma_0 + 2(\gamma_0 \gamma_s^d)^{1/2} \qquad (1)$$

where π_s is the spreading film pressure (equal to the work of spreading wetting W_s) and γ_0 is the surface tension of n-octane ($\gamma_0 = \gamma_0^d = 21.8 \text{ mN m}^{-1}$). Calculated values are listed in Table II, from which a slight increase of the dispersive component of surface free energy with increasing time of the thermal treatment can be seen.

Fig. 4 shows the dependence of nitromethane film pressure as a function of its statistical monolayers for glasses I and IV. Next, the non-dispersive component (γ_s^n) of the surface free energy was calculated from the film pressure values appearing at the inflexion points for the 4th and 6th monolayers [19, 20, 33]:

$$\pi_s = W_s = -2\gamma_n + 2(\gamma_n^d \gamma_s^d)^{1/2} + 2(\gamma_n^n \gamma_s^n)^{1/2} \qquad (2)$$

where γ_n is the surface tension of nitromethane ($\gamma_n = 36.2 \text{ mN m}^{-1}$), γ_n^d is the dispersive part of the nitromethane surface tension ($\gamma_n^d = 31.96 \text{ mN m}^{-1}$), and γ_n^n is the non-dispersive part ($\gamma_n^n = 4.24 \text{ mN m}^{-1}$).

The dispersive components of surface free energy for glasses I to IV determined above were employed for the calculation of γ_s^n. The calculated non-dispersive component values for glasses I–IV are also collected in Table II.

The calculated data show a significant decrease in the non-dispersive component of surface free energy as the result of glass heating. From these results it can be concluded that the longer the thermal treatment, the more hydrophobic is the CPG surface [34].

From our previous studies [10] it emerged that for a prolonged time of thermal treatment an increase of adsorption takes place for unmodified CPG. It is well known that a polar CPG surface adsorbs water from the environment both quickly and strongly. During the deposition of organic liquids on to CPG surfaces, the surfaces were in contact with the surrounding air. Moreover, the applied liquids (n-octane and nitromethane) were not dried before deposition. Taking these facts into account, it can be concluded that the calculated values refer rather to CPG with adsorbed water molecules or possessing a water film whose properties are dependent on the supporting sur-
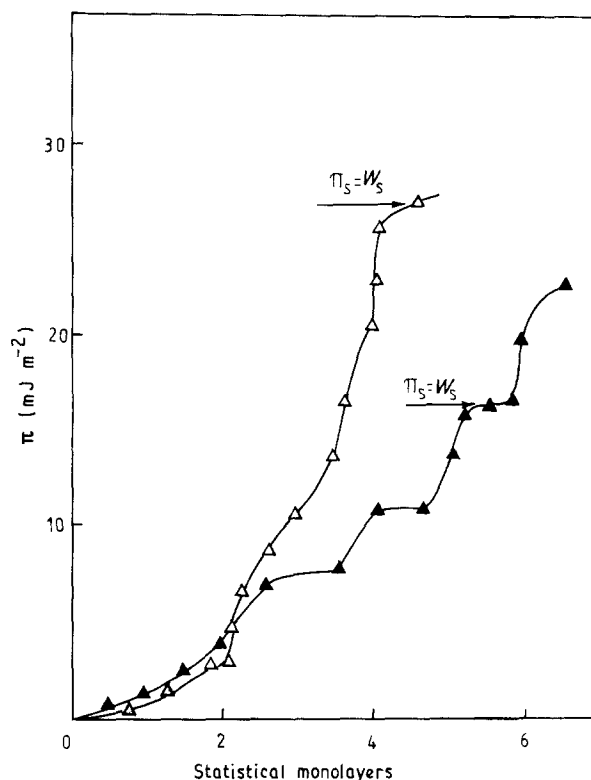

Figure 4 The same relationships as in Fig. 3 for nitromethane: ($\triangle$) glass I, ($\blacktriangle$) glass IV.

face properties (CPG I–IV). This suggestion is confirmed by changes in γ_s^d and γ_s^n between a bare quartz surface and one covered with a single monolayer water film [31, 35]. They are equal respectively to $\gamma_s^d = 76 \text{ mJ m}^{-2}$, $\gamma_s^n = 115 \text{ mJ m}^{-2}$ and $\gamma_s^d = 29.7 \text{ mJ m}^{-2}$, $\gamma_s^n = 91.3 \text{ mJ m}^{-2}$. The values of the surface free energy components for untreated CPG I are similar to the values for a quartz surface with two monolayers of water [31, 35].

Assuming that the water film pressure on a CPG I surface is equal to the work of spreading wetting, the calculated values of the surface free energy for this glass was decreased by the presence of this film [36]. Based on this assumption the components of surface free energy were recalculated for the bare surface, and they were $\gamma_s^d = 59.2 \text{ mJ m}^{-2}$ and $\gamma_s^n = 149.7 \text{ mJ m}^{-2}$.

Using the same assumption, the components of the surface free energy for CPG II would be equal to $\gamma_s^d = 64.16 \text{ mJ m}^{-2}$ and $\gamma_s^n = 65.45 \text{ mJ m}^{-2}$. There is no justification for performing such calculations for glasses III and IV because water can only decrease the polar component of CPG to 51 mJ m^{-2}.

From the above it appears that untreated glass is more polar than quartz is. The latter study has been documented in the literature resulting from the presence of polar and active centres stronger than SiOH groups [10, 11]. More difficult is an interpretation of the γ_s^n values for CPG II–IV presented in Table II.

According to the literature, several processes occurs on the surface of thermally treated CPG [5, 10, 24, 26, 37, 38]:

(i) dehydroxylation of siliceous areas of the CPG surface which are not covered by boron atoms,

TABLE II Changes of γ_s^d and γ_s^n for investigated CPGs

Glass No.	Components of surface free energy (mJ m^{-2})			
	Non-silanized		Silanized	
	γ_s^d	γ_s^n	γ_s^d	γ_s^n
I	31.32	76.95	36.71	41.15
II	32.95	51.9		
III	33.96	35.69		
IV	35.08	27.24	45.8	8.9

(ii) enrichment of the CPG surface in boron atoms (diffusion from bulk to the surface) and rehydroxylation of these surface areas (to which boron atoms have diffused),

(iii) diffusion of sodium ions towards the CPG surface,

(iv) crystallization of the siliceous CPG skeleton, and

(v) formation of borate clusters on the CPG surface for a suitably long time of treatment.

All these processes may account for the diminution of γ_s^n for glasses II–IV. A short period of heating (see glass II) causes mainly a surface dehydroxylation process, (diffusion of sodium and boron is significantly slower) and hence a decrease of γ_s^n to $51.9 \, mJ \, m^{-2}$. A longer period of heating (glasses III and IV), besides dehydroxylation, is also associated with an enrichment of the surface with boron and sodium atoms and the formation of borate clusters on the CPG surface, which both increase the hydrophobicity of the CPG surface and decrease γ_s^n to $35.69 \, mJ \, m^{-2}$ for CPG III, and to $27.24 \, mJ \, m^{-2}$ for glass IV.

As shown previously [10, 37], the more active boron atoms and B–OH groups in relation to silanol groups increase the CPG adsorption properties when the thermal treatment time increases. The presence of a water film and its influence on the surface free energy also cannot be excluded. A possible appearance of water can result in the formation of micro-drops (but not a uniform layer) [39] existing on certain surface-energetic heterogeneities (patches). The latter can be deduced from the spreading coefficients for glasses III and IV, which (according to Equation 2) equal -5.9 and $-16.6 \, mJ \, m^{-2}$, respectively.

The literature data also point to the existence of B–O–B bridges on thermally treated CPG surfaces [11, 12]. Due to electron deficiency there are strong adsorption centres of the Lewis type.

CPGs very often serve as supports for chemically bonded phases. In particular, sorbents composed of CPG and γ-aminopropyl radicals chemically bonded with them are readily applied in biochemical and biotechnological laboratories and in industry. As can be expected, the chemical properties of the initial support are changed by chemical modification. This is confirmed by Table I, which contains specific surface areas of the materials investigated. From Table I it is seen that S_{BET} for modified CPG decreases in comparison with the untreated CPG.

Table I also shows the coverage densities of the investigated silanized materials. As can be seen, thermal treatment leads to a slight decrease of the number of radicals chemically bonded with the CPG surface unit. It is worth noting that CPG was not rehydroxylated before the bonding procedure. The amount of bonded APTES radicals indicates a similar amount of hydroxyl groups on CPG I and IV surfaces.

In order to obtain more information about porous glasses with chemically bonded γ-aminopropyl radicals, the components of surface free energy were measured using the same procedure as in the case of non-modified CPG. The zeta potentials versus the

volume of deposited n-octane and nitromethane are shown in Figs 5 and 6, respectively. Statistical monolayers of the liquids, calculated as above, are marked by vertical dashes. It appears from a comparison of the curves presented that both materials (CPG I–APTES and CPG IV–APTES) show a similar behaviour.

The film pressure versus the number of statistical monolayers for n-octane and nitromethane on CPG I–APTES and CPG IV–APTES are presented in Figs 7 and 8, respectively. As can be seen (Fig. 7), an analogous course of changes of the n-octane film pressure has been obtained. The inflexion points corresponding to 2.6 monolayers were taken as giving π_s. Dispersive interactions of surface free energy were calculated from Equation 1. The data obtained for the dispersive component are shown in Table II. In both cases the increase of dispersive interaction was probably connected with the formation of a polymeric compound on the CPG surface. The presented γ_s^d values are close to the dispersive component of surface free energy cited in the literature for polymers [1–3, 17, 18].

Fig. 8 shows the changes of the film pressure of nitromethane for the CPG–APTES system as a function of the number of nitromethane monolayers. Taking the γ_s^d values calculated above for modified glasses, the non-dispersive components of surface free energy were calculated by taking the π values at the first inflexion point occurring at 2.6 monolayers. These values are collected in Table II. As seen from
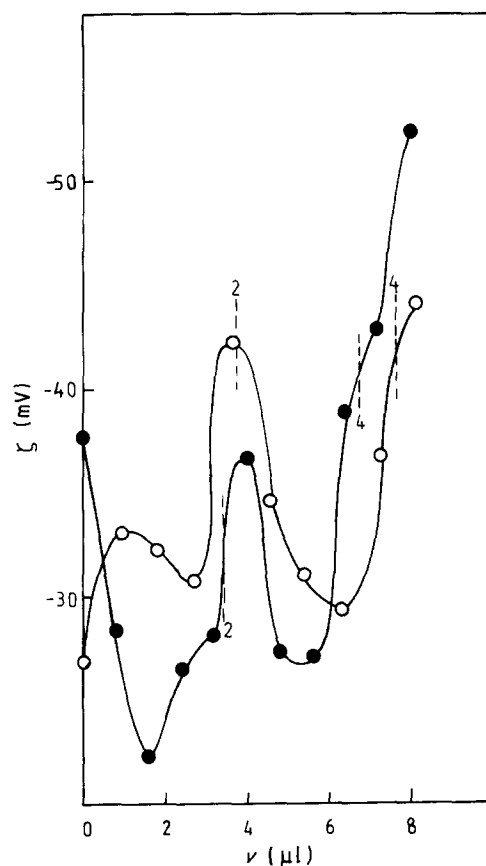

Figure 5 Changes of ζ potential of (○) glass I and (●) glass IV coated with APTES as a function of n-octane coverage.
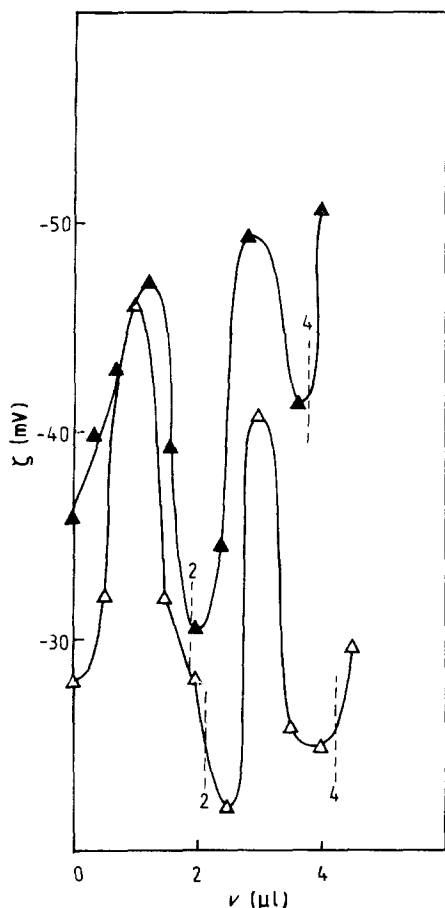
Figure 6 The same relationships as in Fig. 5 for nitromethane: (△) glass I, (▲) glass IV.
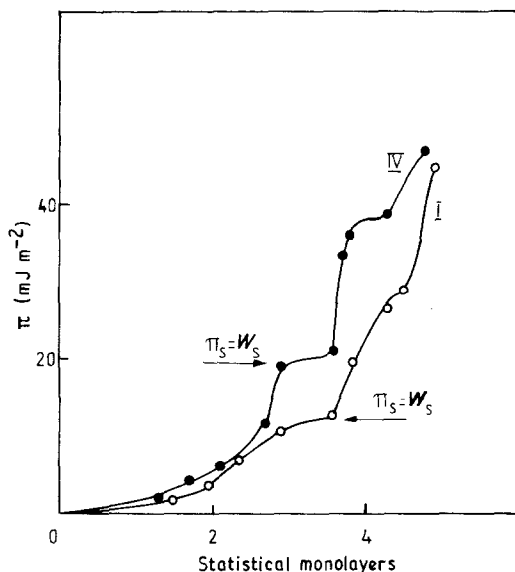

Figure 7 Film pressure π of n-octane for (○) glass I and (●) glass IV coated with APTES as a function of the number of n-alkane calculated monolayers.

these data, the chemical bonding of γ-aminopropyl-triethoxysilane to CPG causes hydrophobicity of its surface. This probably results from the replacement of surface hydroxyl groups by γ-aminopropyl radicals. The percentage of the hydrophobicity increase, expressed as the decrease in the non-dispersive compon-
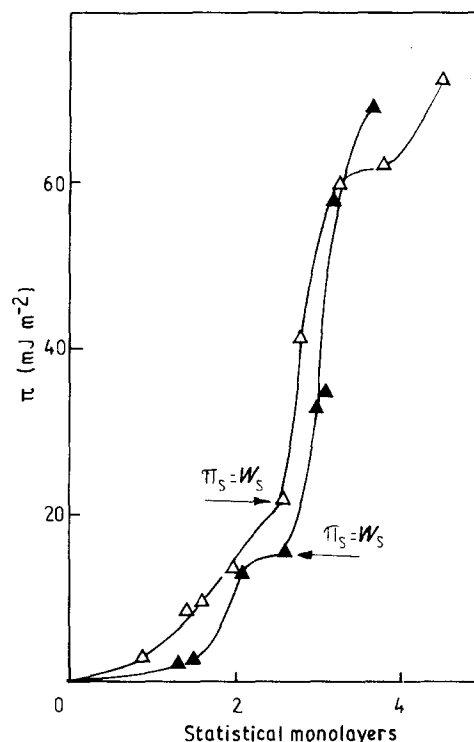

Figure 8 The same relationships as in Fig. 7 for nitromethane: (△) glass I, (▲) glass IV.

ent of surface free energy, is the same in both cases. Glasses I and IV possess a similar coverage density by OH groups. The decrease of γ_s^n for heated glasses does not only result from dehydroxylation but also from the other processes mentioned above.

4. Conclusions

1. Zeta potential changes for the tested glasses in water as a function of the surface coverage with n-octane and nitromethane are neither linear nor mono-tonic. The zeta potentials oscillate, showing maxima and minima, and the extrema tend to decrease with a prolonged heating time; this is connected with changes of the electric surface charge on the CPG surface.

2. In all cases the zeta potential is characterized by negative values. This is connected with an accumulation of excess negative charge in the slipping plane. It can be assumed that the negative values of the electrokinetic potential result from the excess of hydroxyl groups on the surface. On the other hand, a well-structured ionic double layer is hardly likely, because there are practically no other ions in the systems studied except H^+ (10^{-6} M) and OH^- (10^{-8} M). Preferential dipole orientation of the adsorbed water molecules should also be taken into account as a factor influencing the changes of the negative zeta potential in the slipping plane.

3. Zeta potentials for APTES-modified glasses are higher than those for the unmodified CPG. An analogous course of the zeta-potential changes was observed for CPG-APTES/n-octane and CPG-APTES/nitromethane systems.

4. Modification of CPG surfaces changed their surface properties, expressed in changes of the surface free energy components:

(i) the dispersive component showed a tendency to increase with prolonged thermal treatment time (from 31.32 mJ m^{-2} for glass I to 35.08 mJ m^{-2} for glass IV);

(ii) dehydroxylation, boron and sodium enrichment and cluster formation on the CPG surface (by thermal treatment) cause a significant decrease of the non-dispersive component of the surface free energy, from 76.95 mJ m^{-2} (or 149.7) for glass I to 27.24 mJ m^{-2} for glass IV. This causes an increase in the hydrophobic character of the modified glasses.

5. It can be expected that the calculated surface free energy components for thermally modified CPG surfaces refer to a surface with adsorbed water molecules or possessing a water film, of a structure which depends on the properties of the CPG surface itself.

6. The APTES modification process leads to an increase of the dispersive interactions. This can be explained by a blocking of negatively charged centres. Thus, the possibility of water-molecule interactions with the polar centres of the support is eliminated. Therefore, a significant decrease in γ_s^n also takes place. During modification, a layer having the character of a polymeric compound might also be formed.

7. The surface free energy components calculated from electrokinetic measurements give information about the physicochemical properties of the sorbent surface, and show the types and magnitude of interactions occurring on the surface. On the basis of the experiments described above and further developments it will probably be possible to choose more easily a suitable sorbent, an optimal stationary phase, a well-wetting support surface and a mobile phase composition, ensuring in this way a good chromatographic resolution for the chromatographed mixture.

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