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Determination of porous glass surface free energy components from contact angles

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The contact angles of water drops and diiodomethane drops on pellets made of controlled porosity glasses have been measured. The surface of the glasses was modified by thermal treatment at 873 K which led to an increase in the surface concentration of boron atoms. Glass modified with Carbowax 20M (polyethylene glycol) and fully hydroxylated glass have also been studied. Using the measured contact angles and modified Young equation, the dispersion and nondispersion components of the glass surface free energy have been calculated. The values show that with increasing heating time (increasing surface density of boron atoms) an increase in the surface polarity takes place. However, the polarity of the same samples decreases after treatment with Carbowax, increasingly so with higher boron atom concentrations.

1. Introduction

The efficiency and the separation process in chromatographic methods is mainly determined by the type of material used as the column packing. Controlled porosity glasses (CPG) as well as silica gels, seems to be very effective column fillings for use in gas and liquid chromatography [1]. The main difference between both materials results from their porous structure and from the boron atoms remaining in the CPG structure after its preparation [2, 3]. The last feature reduces the use of porous glasses especially for the separation of proteins [4].

Surface properties of the porous glasses first depend upon the number of –OH groups bounded to silicon or boron atoms (Si–OH or B–OH groups) [2, 5–7]. From spectroscopic studies it is found that on the porous glass surface, not thermally treated, there are about three times more silicon than boron atoms [5]. Thermal treatment of the glasses, on the one hand, leads to dehydroxylation of the silicon groups, and on the other hand, causes diffusion of the boron atoms towards the surface from the interior of the material and then the creation of B–OH groups [2, 5–7]. For prolongated thermal treatment of the sample more and more boron atoms occupy the surface and some B–OH groups become dehydroxylated [6].

Some authors suggest that after long thermal exposure boron can form B_2O_3 clusters on the surface [7, 8]. The presence of the hydroxyl groups and surface boron atoms causes the glass surface to become polar. Polar interactions between the glass surface and molecules of the separated substances are not often advantageous [4] for the chromatographic separation process. To avoid the problem, the glass surface to be used is modified by chemical bonding of silanes, Carbowax or by phase deposition onto it [9, 10]. Chemically bonded phases do not always give a satisfactory result because some of the surface boron atoms may still remain unbound.

One parameter by which the glass surface properties can be controlled is their surface free energy. The energy can be expressed by the sum of the dispersion and nondispersion components resulting from various intermolecular interactions. However, in the literature few data dealing with this subject are available. Therefore, it seemed interesting, both from the practical as well as the theoretical view points, to determine the dispersion and nondispersion components of the surface free energy of the porous glasses. The samples were treated thermally for various periods of time and their surfaces were also modified using Carbowax 20M (polyethylene glycol) deposition. The surface free energy components were determined by wetting contact angle measurement.

2. Theory

For more than 25 years the surface free energy of liquids and solids has been considered by many authors to be represented by the sum of several components resulting from various types of intermolecular interactions [11–17]. Namely, dispersion–London's type (d), dipole–dipole (p), dipole–induced dipole (i), hydrogen bond (h), π-bonds (π), donor–acceptor (ad), and electrostatic (e). Thus for a solid or liquid the surface free energy can be written as

$$\gamma = \gamma^{d} + \gamma^{p} + \gamma^{i} + \gamma^{h} + \gamma^{\pi} + \gamma^{ad} + \gamma^{e} \quad (1)$$

where γ is the surface free energy and the superscripts denote the kind of interactions.

Depending on the specific nature of the substance, only one, two or more types of interaction operate across the interface. For practical purposes, Equation

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1 is frequently used in a more simplified form [11]

$$\gamma = \gamma^d + \gamma^n \qquad (2)$$

where superscript n represents all nondispersion interactions which contribute to the experimentally determined value. Thus, in Equation 2 the surface free energy is treated as a magnitude consisting of two components, dispersion and nondispersion. Unfortunately, there are no direct methods by which the components may be determined, especially for solids. For this purpose various methods, based on adsorption measurements, are applied [11]: heat of wetting [11], zeta potential measurements [18, 19], and wetting contact angle measured in specially chosen systems [11–17, 20–22]. Methods based on the contact angle are the most frequently used for solid surface free energy component determination. However, to obtain realistic values of the components, the liquids used for contact angle measurements should be very carefully selected and the measured contact angles require proper interpretation. Fulfilment of both these conditions is sometimes very difficult, especially in the case of high energetic polar solids. The porous glasses are one case. Usually a strongly bonded water film is present on the surface of such solids which can be removed from the surface only by heating the sample at a high temperature.

Studies conducted in our Laboratory on the surface free energy of quartz and marble [23] and low-energy polymeric solids [20] have shown that water and diiodomethane are very useful liquids for surface free energy component determination from contact angle measurements. Water is a polar liquid having a high surface tension ($72.8\,\mathrm{mN\,m^{-1}}$) [11] originating in 30% from dispersion and in 70% from nondispersion interactions [20], whereas diiodomethane is an apolar liquid having one of the highest surface tensions ($50.8\,\mathrm{mN\,m^{-1}}$) [24] that in 99.3% results from the dispersion interactions [20].

The equilibrium state in the system of interest, porous glass–water drop–air and porous glass–diiodomethane drop–air, can be described on the basis of the Young equation

$$\gamma_{\mathrm{sf}_1} - \gamma_{\mathrm{sfW}} = \gamma_{\mathrm{W}} \cos\theta_{\mathrm{W}} \qquad (3)$$

$$\gamma_{\mathrm{sf}_2} - \gamma_{\mathrm{sfD}} = \gamma_{\mathrm{D}} \cos\theta_{\mathrm{D}} \qquad (4)$$

where γ_{sf} is the surface free energy of the porous glass covered with a strongly bonded water film, γ_{sf_1} is the surface free energy of the porous glass with a strongly bonded water film on which there is a less-ordered water film around the drop, γ_{sf_2} is the surface free energy of the glass covered with a water and diiodomethane film, γ_{W} is the surface tension of water, γ_{D} is the surface tension of diiodomethane, θ_{W} is the contact angle of water, θ_{D} is the contact angle of diiodomethane, γ_{sfW} is the interfacial free energy of the glass/water film–water and γ_{sfD} is the interfacial free energy of the glass/water film–diiodomethane. Assuming that, $\gamma_{\mathrm{sf}_1} = \gamma_{\mathrm{sf}} - \pi e_1$ and $\gamma_{\mathrm{sf}_2} = \gamma_{\mathrm{sf}} - \pi e_2$ and expressing γ_{sfW} and γ_{sfD} as a function of dispersion [11, 16] and nondispersion [12–17] interfacial interactions, from Equations 3 and 4 we obtain

$$\gamma_{\mathrm{W}} \cos\theta_{\mathrm{W}} = -\gamma_{\mathrm{W}} + 2(\gamma_{\mathrm{sf}}^{\mathrm{d}}\gamma_{\mathrm{W}}^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{sf}}^{\mathrm{n}}\gamma_{\mathrm{W}}^{\mathrm{n}})^{1/2} - \pi e_1 \qquad (5)$$

$$\gamma_{\mathrm{D}} \cos\theta_{\mathrm{D}} = -\gamma_{\mathrm{D}} + 2(\gamma_{\mathrm{sf}}^{\mathrm{d}}\gamma_{\mathrm{D}}^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{sf}}^{\mathrm{n}}\gamma_{\mathrm{D}}^{\mathrm{n}})^{1/2} - \pi e_2 \qquad (6)$$

where $\gamma_{\mathrm{W}}^{\mathrm{d}}$ and $\gamma_{\mathrm{W}}^{\mathrm{n}}$ are the dispersion and nondispersion components of the surface tension of water and $\gamma_{\mathrm{D}}^{\mathrm{d}}$, $\gamma_{\mathrm{D}}^{\mathrm{n}}$ are the components of the diiodomethane, $\gamma_{\mathrm{sf}}^{\mathrm{d}}$, $\gamma_{\mathrm{sf}}^{\mathrm{n}}$ are the surface free energy components, dispersion and nondispersion, of the porous glass with strongly bonded water film, πe_1 is the difference between the surface free energy of the porous glass under the water drop and behind the drop, and πe_2 is the difference in energy for the diiodomethane drop.

Using Equations 5 and 6 and measuring θ_{W} and θ_{D} it is possible to calculate the components of the surface free energy of the glass for several cases, when the surface free energy of the porous glass with a strongly bonded water film is the same under water and diiodomethane drops, and

(i) $\pi e_1 = 0$ and $\pi e_2 = 0$, or
(ii) $\gamma_{\mathrm{sf}_1} \to \gamma_{\mathrm{W}}$ and $\pi e_2 = 0$, or
(iii) $\pi e_1 = 0$ and $\gamma_{\mathrm{sf}_2} \to \gamma_{\mathrm{D}}$, or
(iv) $\gamma_{\mathrm{sf}_1} \to \gamma_{\mathrm{W}}$ and $\gamma_{\mathrm{sf}_2} \to \gamma_{\mathrm{D}}$.

3. Experimental details

Contact angle measurements on the porous glasses were made using a sessile drop method [25] at $293 \pm 0.1\,\mathrm{K}$ using a telescope–goniometer set with × 25 magnification. The porous glass (NS) employed for the measurements, possessing pores of 20 nm diameter and a boron content of 3.1%, was treated thermally at 872 K for 5 (NS + 5) or 110 (NS + 110) h and was also modified by the deposition of Carbowax, thus obtaining samples denoted NS + C, NS + 5 + C, NS + 110 + C. Details of the glass preparation have been described earlier [26, 27].

As mentioned above, the longitudinal thermal treatment leads to dehydroxylation of part of the surface. For this reason the sample NS + 110 was also hydroxylated according to the procedure described in [27] (sample NS + 110 H).

To measure contact angles, pellets were prepared from the powders using a press. The powders were pressed under a pressure of $12\,000\,\mathrm{kg\,cm^{-2}}$. The powder was placed in a stainless steel container with a finely polished bottom. A polyethylene foil was placed between the piston and powder. The foil strengthened the pellet. Using pellets thus prepared, contact angles were measured in the following systems: glass–water drop–air and glass–diiodomethane drop–air.

In the case of water drops the measurements were made as follows: the glass pellets were placed in the measuring chamber which was filled with saturated water vapour. After 30 min a water drop, of volume $2\,\mathrm{mm^3}$, was settled on the pellet surface with the help of a microsyringe and the contact angle was read immediately on both sides of the drop. If the values differed by more than 2° they were not taken into account. At least 5 pellets of the same type of the porous glass were employed for contact angle

TABLE I Contact angles of water drop (θ_W) and diiodomethane drop (θ_D) on the pellets of porous glasses, and the dispersion (γ_{Sf}^d) and nondispersion (γ_{Sf}^n) components of the glass surface free energy

Porous glass	θ_D (deg)	θ_W (deg)	γ_{Sf}^d* (mJ m^{-2})	γ_{Sf}^n* (mJ m^2)	$\gamma_{Sf_I}^d$† (mJ m^{-2})	$\gamma_{Sf_I}^n$† (mJ m^{-2})
NS	26.2	37.7	34.15	117.96	40.39	24.75
NS + 5	26.8	38.8	33.83	120.66	40.23	24.23
NS + 110	29.7	44.2	32.26	133.88	39.45	21.57
NS + 110 H	29.8	54.3	31.25	157.94	40.20	15.41
NS + C	25.3	24.2	36.05	86.40	39.99	31.49
NS + 5 + C	24.5	21.6	36.69	79.68	40.17	32.40
NS + 110 + C	21.4	17.3	38.49	65.68	41.04	33.35

*Equations 5 and 6
†Equations 7 and 5.

determinations and two or three drops were settled on each pellet. The average contact angle was calculated from all the readings, using only values which differed by no more than 4°. About 90% of the values fitted the condition. The contact angle measurements for diiodomethane drops were conducted in a similar way with the exception that the chamber was "dried" to remove water vapour with the help of molecular sieves (4Å + 5Å) before the pellets were placed inside it. The accuracy of the contact angle measurements was ± 1°.

4. Results and discussion

Values of the measured contact angle are listed in Table I. They show that heating of the glass for 0 to 110 h (thus increasing the density of surface boron atoms [26, 27]) leads to only a slight increase in the contact angle, from 26.2° to 29.7°, i.e. by 3.5° in the case of the diiodomethane drop. In the case of the water drop, the angle also increases from 37.7° to 44.2°, i.e. by 6.5°. Modification of the glass surface with polyethelene glycol (Carbowax 20M) makes the surface slightly more wettable by the diiodomethane drop, and markedly more wettable by water. For non-thermally treated glass samples, modification with Carbowax produced a change in contact angle for the diiodomethane drop, θ_D, from 26.2° to 25.3°, and for the water drop, θ_W, from 37.7° to 24.2°. In the case of sample enrichment with boron atoms (heated for 110 h at 873 K) and then covering with Carbowax, the contact angle decreased further, to 21.4° for diiodomethane, and to 17.3° for water. It is characteristic that the highest contact angle values, both for diiodomethane and water were found for the glass sample with the highest concentration of boron atoms (NS 110 h heating) and then hydroxylated NS + 110 H; they were 29.8° and 54.3°, respectively. The contact angle value for water (54.3°) is nearly equal to that found for water on quartz [28].

Taking measured values of θ_D and θ_W from Equations 5 and 6 the dispersion and nondispersion components of the CPG samples can be determined. However, it is only posible if πe_1 and πe_2 values are defined. Because the porous glass can be regarded as high energetic solids it is improbable that diiodomethane molecules, possibly adsorbed around its drop settled on the surface, could change the glass surface free energy. As already mentioned, diiodomethane is a nonpolar, high-energetic organic liquid, having a low vapour pressure at the temperature of the measurements (293 K). On polar solids the spreading coefficient for diiodomethane is negative. It is hardly possible to assume that this liquid blocks the polar interactions present on the glass surface, especially taking into account the experimental conditions. The diiodomethane molecules could be adsorbed on the hydrophobic centres of the glass surface, thus reducing the dispersion component, if the component was higher than γ_S^d [11].

Recognizing the above and assuming that $\gamma_{Sf}^d < \gamma_S^d$, it is reasonable that $\pi e_2 = 0$. In the system CPG–water drop–air the possibility cannot be excluded that the glass surface free energy is decreased by water molecules being adsorbed on the surface around the water drop, and moreover, that contact angles were measured in the presence of saturated water vapour.

Our earlier studies on wettability [28, 29] under similar conditions, of quartz have shown that the adsorbed water film probably decreases their surface free energy behind the water drop, up to the surface tension of water. Recognizing the case for a porous glass surface, in Equation 5 $\pi e_1 = \gamma_{Sf} - \gamma_W$. So, using measured contact angles θ_W and θ_D, and taking the literature values for γ_W, γ_W^d, γ_W^n [11], γ_D [24], γ_D^d and γ_D^n [20], listed in Table II, for $\pi e_2 = 0$, $\pi e_1 = \gamma_{Sf} - \gamma_W$, from Equations 5 and 6 the dispersion and nondispersion components of the surface free energy for tested samples of CPG have been calculated. These values are listed in Table I. This Table also gives values of the components calculated from Equations 7 and 5 obtained assuming that πe_1 can equal zero: this case can be expected for $\gamma_{Sf} < \gamma_W$, then

$$(\gamma_{Sf}^d)^{1/2} = \frac{50.8\,(1 + \cos\theta_D) - 6.284\,(1 + \cos_W)}{13.395} \tag{7}$$

Equation 7 follows from Equations 5 and 6 after introducing into them the values of γ_W, γ_W^d, γ_W^n, γ_D, γ_D^d and γ_D^n given in Table II.

On analysing the results presented in Table I, it

TABLE II Literature values of surface tension (γ_L) of water and diiodomethane and the dispersion, γ_L^d, and nondispersion, γ_L^n, components of the tension [11, 15, 24]

Liquid	γ_L	γ_L^d (mN m^{-1})	γ_L^n (mN m^{-1})
Water	72.8	21.80	51.00
Diiodomethane	50.8	50.42	0.38

can be stated that with increasing time of glass heating (enrichment of the surface with boron atoms) the dispersion component of the surface free energy does not change meaningfully, only from 34.15 to 32.26 mJ m^{-2}. On the other hand, for the same samples of glass the nondispersion component changes from 117.86 to 133.88 mJ m^{-2}. Deposition of Carbowax also causes only a slight increase in the dispersion component and a marked decrease in the nondispersion component, i.e. $\gamma_{\mathrm{sf}}^{\mathrm{d}} = 36.05$ (for NS + C) and $\gamma_{\mathrm{sf}}^{\mathrm{d}} = 38.49$ (for NS + 110 + C), while $\gamma_{\mathrm{sf}}^{\mathrm{n}} = 86.4$ (for NS + C) and $\gamma_{\mathrm{sf}}^{\mathrm{n}} = 65.68$ (for NS + 110 + C) (all values in mJ m^{-2}).

From Table I it also results that $\gamma_{\mathrm{sf}}^{\mathrm{d}}$ values can be put in the following sequences:

(i) NS > NS + 5 > NS + 110
(ii) NS + C < NS + 5 + C < NS + 110 + C
(iii) NS + 110 + C > NS + 110 H.

The values of the nondispersion component $\gamma_{\mathrm{sf}}^{\mathrm{n}}$ follow quite opposite sequences.

It should be stressed that values of $\gamma_{\mathrm{sf}}^{\mathrm{d}}$ calculated from Equation 7 practically do not differ among themselves and are higher than those discussed above. The values of $\gamma_{\mathrm{sf}}^{\mathrm{d}}$ obtained from this equation lie between 15.41 and 24.75 mJ m^{-2}. These values suggest that the second model used for the calculations is less probable and will not be discussed further here. Thus, considering $\gamma_{\mathrm{sf}}^{\mathrm{d}}$ and $\gamma_{\mathrm{sf}}^{\mathrm{n}}$ values calculated from Equations 5 and 6 and for $\pi e_1 = \gamma_{\mathrm{sf}} - \gamma_{\mathrm{W}}$ and $i\pi e_2 = 0$ as those more reliable, it can be stated that with increasing density of boron atoms on the CPG surface, its polarity increases by about 13.5% when the B_2O_3 surface density increases from 0.09 μg m^{-2} to $\sim$200 μg m^{-2} [30, 31] (NS → NS + 110). This is due to boron diffusion and B–OH group formation on the surface, despite the fact of some silanol groups dehydroxylate which become hydrophobic siloxane groups.

Contact angles of water drops found on CPG NS, and NS + 110 increase by 16. 6° from 37.7° for NS to 54.3° for NS + 110. This last value is similar to that found on thermally heated quartz 52° to 54° [28]. In the case of quartz, it was assumed that under normal conditions its surface free energy determined experimentally concerned the surface, covered with a water film. Heating of the surface causes, to some extent, progressive destruction of the strongly bonded water film and hence an increase in the polar component of the surface free energy. This may also be the case for the porous glasses, which is an additional effect to that of boron atoms causing the observed increase in $\gamma_{\mathrm{sf}}^{\mathrm{n}}$ values (Table I). The results of $\gamma_{\mathrm{sf}}^{\mathrm{n}}$ obtained for the same samples of the glass but additionally treated with Carbowax verify the above ideas. Because the glass surface enriched with boron atoms becomes more hydrophilic due to the presence of B–OH groups, more Carbowax molecules can be deposited on the surface [26] making it less polar and more hydrophobic, in excellent agreement with the results shown in Table I for NS (+5, +110) + C samples. The polarity of the sample NS + 110 + C15 about 24% less than that of NS + C and about 100% less than NS + 110.

The fact that the surface density of -OH groups determines the surface polarity clearly shows results obtained for $\gamma_{\mathrm{sf}}^{\mathrm{n}}$ for the glass surface additionally hydroxylated, and with high content of boron atoms NS + 110 H (Table I), for which the nondispersion component is 157.9 mJ m^{-2} and is about 34% higher than that of nontreated (NS) porous glass samples, and about 18% higher than that for NS + 110.

The results presented seems to give better insight into the surface properties of porous glasses and should be helpful in anticipating the separation properties of these materials.

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