

Surface free energy of smooth and dehydroxylated fused quartz from contact angle measurements using some particular organics as probe liquids

I. ZGURA^a, R. MOLDOVAN^b, C. C. NEGRILA^a, S. FRUNZA^a, V. F. COTOROBAI^a, L. FRUNZA^a

^aNational Institute of Materials Physics, PO Box Mg-07, 077125 Magurele, Romania

^bCenter for Advanced Studies in Physics of the Romanian Academy, R-076117 Bucharest, Romania

The dispersion and the polar independent contributions to the surface free energy in the case of fused quartz plates were evaluated by contact angle measurements against a series of liquids like water, glycerol, ethylene glycol, dimethyl sulfoxide and a nematic mixture NP5 of azoxybenzene type compounds. The smooth fused quartz plates were thermally pretreated at 240°C and 1000°C to decrease the number of surface hydroxyl groups; their surface was characterized by X-ray photoelectron spectroscopy. The contact angle data were further processed applying either the approach of Owens-Wendt with geometric mean or the Wu's approach of harmonic mean of nonpolar and polar interactions. The liquids were chosen thus to fulfill Della Volpe and Siboni's criterion namely that these have the condition number of system matrix low enough. The values obtained for the components of surface free energy were discussed in comparison with the results obtained in literature for crystalline quartz or for other silica forms as bulk or films. The study has shown a decrease of the polar component of the surface tension by increase of the pretreatment temperature.

(Received April 12, 2013; accepted July 11, 2013)

Keywords: Surface free energy, Surface tension, Contact angle, Fused quartz, Owens-Wendt model, Wu model

1. Introduction

Interfacial free energy interactions are important in many surface and interface processes, especially those met in micro-/nanotechnology [1]. These characteristics of a solid can be quantified by the surface free energy (SFE) which made the subject of intense research for over fifty years. Among the methods developed to evaluate SFE, those based on the contact angle measurements are the most used because of a relative ease in performing the measurements [2]. These measurements are then performed on the surface of the investigated material against a series of probe liquids, usually water and/or known organic solvents.

Quartz either crystalline or in a glassy state is nowadays a widely used material due to its properties as strength, thermal stability, UV transparency and chemical inertia to most elements and compounds. That is why it is an excellent substrate for projection masks; it has industrial applications in the fabrication of semiconductors, surface mirrors, resonators, various refractory shapes for high-temperature thermal processes, laboratory glassware. Quartz found applications even in textile processes such as beaming, weaving, braiding, texturizing, knitting, etc. It is also a model in surface science. Water molecules are adsorbed on its surface since it is a high-energy hydrophilic solid: The water film can be desorbed by proper thermal treatment, but the thermal treatment can also cause surface dehydroxylation with the formation of siloxane bonds: the quartz surface becomes less hydrophilic.

Measuring the surface tension of quartz has been the subject of a rather high number of specific experimental studies (e.g. [3-14]) sometimes leading to controversial results: However, fewer investigators speak about the polar and dispersive parts of the surface tension. That is why in this paper we focus on the evaluation of the components of SFE for fused quartz plates treated by baking in air at 240°C and 1000°C. These treatment temperatures are those when the dehydroxylation starts and ends respectively [3]. Fused quartz is close to be a structurally isotropic material despite the vacancies and dislocations which change the structure of the (surface) crystals. In fact, one can speak about some local chemical heterogeneity which makes the surface more complex and real at the same time [15]. The contact angles made by water and several non-hydrolysable liquids: glycerol, the liquid crystal mixture NP5, ethylene glycol and dimethyl sulfoxide were measured. From these liquids some were able to spread spontaneously on water/polar surfaces due to the formation of hydrogen bonds [16]. To calculate the surface free energies we have used Owens-Wendt [17] and also Wu [18] methods. The obtained values showing the large contribution to the SFE of the polar part as compared to the dispersion part and are smaller than those reported before. The high temperature treatment leads to the diminution of SFE values on fused quartz while the weight of the dispersion part increases.

2. Approaching Method

The approaching method launches from the plausible supposition (see in the experimental part the deviations from the static values of the contact angle) that the surface of the fused quartz is less chemically and physically heterogeneous: Then, the ideal Young equation (see for example Ref. [19]) can be applied in which the expression of interfacial tension is introduced as follows:

The surface tension γ of the solids and liquids might be divided into additive independent contributions, associated with specific interactions [20]. In the following two contributions will be considered that dispersive γ^d and the other γ^p , of polar nature, according to Owens and Wendt's hypothesis [17]:

$$\gamma = \gamma^d + \gamma^p \quad (1)$$

Taking into account these components, the surface tension of two phases (denoted 1 and 2) in contact is given by the following expression:

$$\gamma_{12} = \left(\sqrt{\gamma_1^d} - \sqrt{\gamma_2^d} \right)^2 + \left(\sqrt{\gamma_1^p} - \sqrt{\gamma_2^p} \right)^2 \quad (2)$$

in the Owens and Wendt's method [21] and by the equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right) \quad (2')$$

in the harmonic mean Wu's method (see Ref. [18] or cited in many works, for example, in Ref. [12]).

In the case of a liquid drop on a solid surface that form a contact angle θ , the general form of the well known Young's equation [22,23] that establishes the balance (see also Figure 1) between the surface tension of the solid γ_S and that of the liquid γ_L and the interfacial tension γ_{SL} is as follows:

$$\gamma_S - \gamma_{SL} - \Pi_{eL} = \gamma_L \cos \theta \quad (3)$$

where Π_{eL} is the pressure of liquid film present on the solid surface due to vapor adsorption.

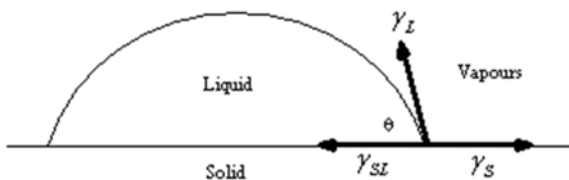


Fig. 1. The equilibrium of interfacial tension forces in the plane of the substrate surface.

Making 1=S and 2=L in eq. (2) one obtains after simple substitutions:

$$\gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_S^d} \sqrt{\gamma_L^d} + 2\sqrt{\gamma_S^p} \sqrt{\gamma_L^p} - \Pi_{eL} \quad (4)$$

or alternatively:

$$\gamma_L (1 + \cos \theta) = 4 \left(\frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \right) - \Pi_{eL} \quad (4')$$

Eqs. (4) and (4') allow evaluating the polar and dispersive parts of the surface tension of the solid knowing these components for several liquids, measuring their contact angles on the solid surface and making at the same time, an adequate assumption relative to the value of Π_{eL} which is zero especially on low energy solids [24] but is commonly assumed zero for such calculations [6].

3. Experimental

3.1. Fused quartz plates

The quartz plates (23 x 32 mm) were cut from a block of high purity optical UV-grade fused quartz, optically polished, carefully cleaned and then rinsed by boiling in monodistilled water and ultrasounding in double distilled water. After drying the plates were treated in oxygen RF plasma for 30 min (in a Standard Plasma Systems, model PICO from Electronic Diener) in order to remove all the traces of organics. The cleaned plates were thermally treated in air for two hours at two temperatures, 240°C and 1000°C. After the quick cooling, the samples were immediately used for contact angle measurements.

The samples to be submitted to XPS analysis were cut to the appropriate size (1x1 cm²) needed for this analysis and then submitted to the same treatment as those prepared for wettability tests.

3.2. Probe liquids

The liquids chosen for contact angle determinations were water (deionised), glycerol (Gly) (99.5%, Sigma Aldrich), a eutectic mixture of liquid crystals with azoxybenzene structure named NP5 (Merck), ethylene glycol (EG) (99%, Chimopar SA) and dimethyl sulfoxide (DMSO) (99.8%, Fisher Scientific). The substances were used without supplementary purification.

3.3. Investigation Methods

XPS was applied to characterize the surface of fused quartz samples. The studies were done with a Surface analysis system (from SPECS) with an X-ray Mg source ($K_{Mg}=1253.6$ eV) working at 300 W; the take-off angle was of 90° and the software, SDP32. Charge compensation was performed with a flood gun operating at 0.1mA and 0.1V. Peak positions were assigned by referencing the C(1s) peak (adventitious carbon) to a binding energy of 285 eV and a linear shift of all other peaks by an equal value, as customary. Both survey and narrow window scans of Si(2p), C(1s), and O(1s) peaks were conducted at 5 eV pass energy for narrow spectra and 50 eV for extended spectra [25]. Fits were carried out for the narrow scan spectra: the line shape, peak width and binding energy

were the adjustable parameters and taking Shirley background. No *in situ* cleaning was applied to the samples before measuring.

Measurements of contact angle on solid substrate was performed from analysis of the profile images of symmetrical static liquid drops using the Drop Shape Analysis System model DSA 100 (Krüss) as previously described (e.g. in Ref. [26, 27]). The sample was placed on the stage, under the tip of liquid-dispensing disposable blunt-end stainless steel needle with outer diameter of 0.5 mm. The needle was attached to a syringe pump controlled by the computer for drop delivery. The volume of the drops was of ca. 2 μ l. The contact angles were determined by fitting the shape of the sessile drop with a smooth curve and then calculating the slope of the tangent to the drop at the liquid-solid-vapor interface line: Low contact angles ($\theta < 30^\circ$) were determined by fitting the shape of the sessile drop with a circle whereas larger contact angles were determined by fitting the drop shape with a polynomial equation of second degree or a circle equation. The camera was positioned to observe the droplet under an angle of about 4° with respect to the sample surface supporting the droplet. The tests were carried out at room temperature. Contact angles were obtained with an uncertainty of $\pm 2^\circ$ from the combined effects of drop asymmetry, surface heterogeneity, and variation in drop position on the plate. At least three determinations were made on the same sample in different areas of the plate surface and the results (for example those presented in Table 1, see below) are mean values.

4. Results and Discussion

4.1. XPS measurements

First of all, the fused quartz surface has been characterized by XPS investigations. The survey spectra are presented in Fig. 2. Beside the peaks characteristic for Si and O, these spectra show only a contamination with carbon which is ubiquitous on practically all materials exposed to ambient conditions. The position of the main Si, C, and O XPS lines are indicated in Fig. 2. Other peaks appearing in the same figure represent Auger lines of O and C and satellites either due to the non-monochromaticity of X-ray radiation or of shake-up type. The carbon contamination decreases dramatically from 11.6 % to 6.9 % after the pretreatment at high temperature.

The atom ratio Si/O for the two samples is 1.77 and respectively 1.75, meaning that the glass surface has a significantly lower oxygen and higher silicon fraction compared to the bulk values which is 1.49. The oxygen fraction increases (a little) after the second heating at 1000°C. An explanation for the latter observation can be the fact that the fraction of oxidized compounds in the adhering carbon layer is increased by the heat treatment or that more free silanol groups were formed on the glass surface after annealing in air and rehydration in ambient atmosphere, this latter hypothesis being less supported. High resolution XP spectra of the sample treated at the two

temperatures are presented in Fig. 3 together with their deconvolution. The Si(2p) and O(1s) binding energies (BEs) found in these fused quartz spectra are in good agreement with the values reported for α -quartz [28, 29]. The total Si(2p) envelop linewidth on fused quartz (ca 1.8 eV) is also similar to, but higher than, that reported previously (1.38-1.42 eV) from a high resolution synchrotron XPS study of a thin noncharging amorphous SiO₂ layer on Si [28, 30]. The Si(2p) line is normally subjected to a spin orbital split (Si(2p_{3/2}) and Si(2p_{1/2})) [28]; however we decided not to discuss this splitting for a simpler presentation.

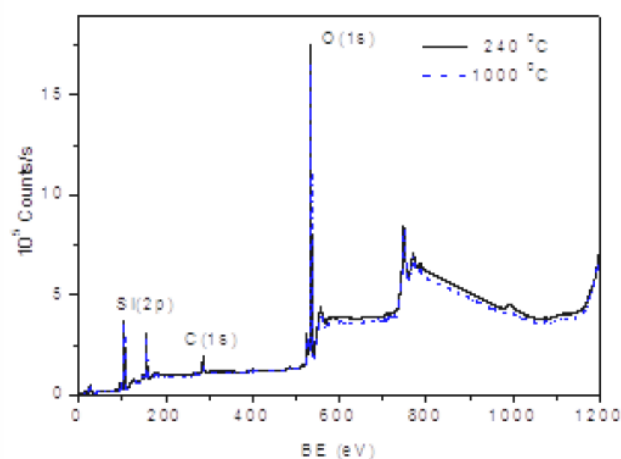


Fig. 2. XPS survey spectra of glass quartz treated at 240°C and 1000°C.

Considering a tetrahedral configuration around silicon atom, the quartz (either crystalline or amorphous) surface might contain several structural entities [31] which represent the basis for the interpretation of the Si(2p) XPS spectrum: Si(Si₄), Si(Si₃O), Si(Si₂O₂), Si(SiO₃) and Si(O₄). However, the fit revealed that the main contributions to the material structure come mostly from two structural entities, one of them leading to the most intense peak. The results are exemplified in Fig. 3, the curves in the upper part. Thus, we found a major component at 102.2 eV and a minor component at 103.3 eV. These components have an approximate ratio of 1:3. The major component shows a lower oxygen coordination (=Si(O)₁₋₂) whereas the component at 103.3 eV shows a higher one (=Si(O)₃₋₄) [32]. Thus, the two components may be assigned to a more glassy and inorganic, silica-like state. According to Miller and Linton [33] the Si binding energy would have to shift to lower values as a result of silanol reaction or condensation. However, it is questionable whether it is generally possible to observe this effect by XPS because of the difficult discrimination of silanol/siloxane bonds using the Si(2p) line.

Detailed analysis of the O(1s) emission peak showed evidence of silanol species (Si-OH) on the surface and the presence of a small amount of non-crystalline, amorphous silica leading to low energy wing of the O(1s) line.

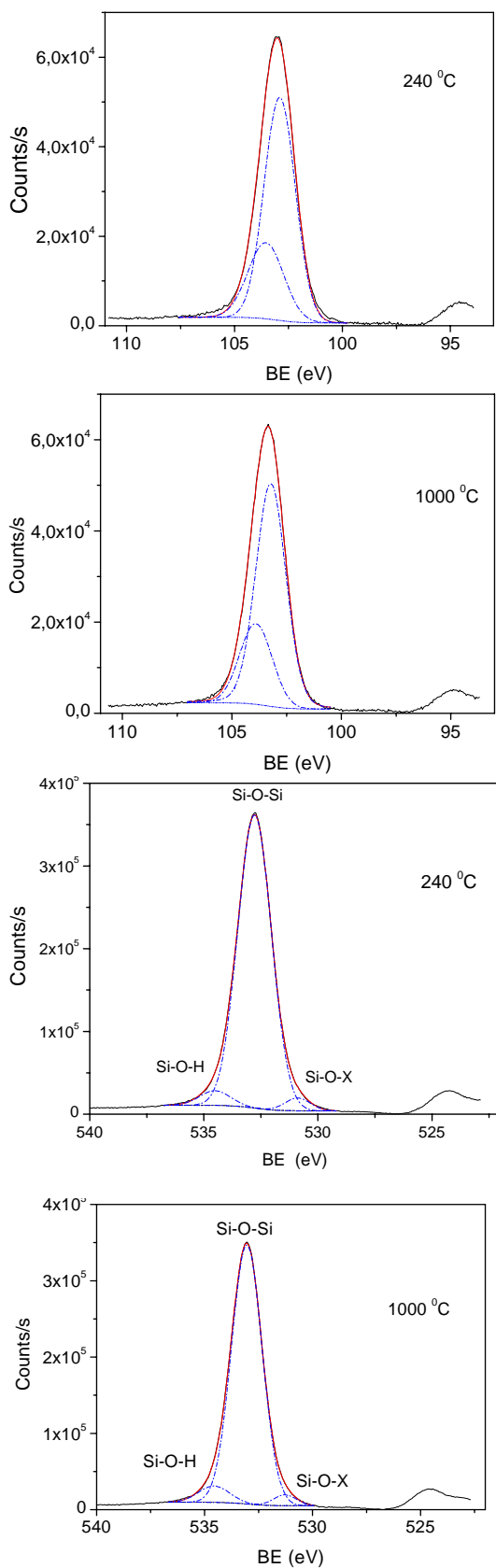


Fig. 3. High resolution XPS spectra of the samples treated at 240 °C and 1000 °C. Upper part: Si(2p) peaks; down part: O(1s) ones. Main components of the spectra and simulated spectra are also shown.

The O(1s) curve fitting of the glass sample yielded a line at 532.77 eV (linewidth of 1.74 eV). This line is dominated by the siloxane component (Si–O–Si). It was not possible to distinguish by XPS the bridges newly formed by rising the baking temperature since the main binding state, as Si–O–Si in the silica glass, are almost identical for the two samples. The smallest peak at 530.89 eV might be assigned to SiO_x species (see e.g. [34]). The peak at 534.52 eV can be well assigned to Si–OH groups [32, 35]: It decreases at 1000°C (6.7%) when compared with the sample treated at 240°C (13.0%).

4.2. Contact angle measurements

We have found contact angles of water on fused quartz in a large interval, the values differing from a sample simply cleaned (76°), to another one supplementary treated with chlorhydric acid (84°), to a sample simply cleaned and additionally washed in ethanol vapors (63°) or to one baked after simple cleaning 1h at 530°C (12°). This behavior is in agreement with that described in the literature, for example with a 20-to-80° range obtained on quartz dehydroxylated by heating, slightly contaminated, or deliberately methylated ([36] or cited in Ref. [37]). The values found by us can be explained by the fact that water contact angles generally depend on the sample purity, on the presence of amorphous materials, on chemical, heating, and other pretreatments and on the contamination by adsorption from laboratory air of substances that could increase the values of the angle. We supposed that the found values depend on the amounts of silanol groups and physically adsorbed water molecules on the quartz/silica surface and proceeded to investigate more “clean” surfaces as obtained by a thermal treatment removing the hydroxyl groups at temperatures of the beginning and ending of the dehydroxylation process [3]. Thus as it was mentioned in Introduction, these temperatures were 240°C and 1000°C and fused quartz plates were baked in air accordingly.

Representative images of the observed water drops on the plates are given in Fig. 4 while the contact angle values measured for all the probe liquids on quartz glass treated by baking in air are given in Table 1.

It is interesting to note that the contact angle obtained for an intermediate treatment at 530°C has an intermediate value between those found at the two temperatures of above despite the fact that different oven were used for the treatment at 530 than that at 240-1000°C.

Table 2 collects a series of properties of the probe molecules which were further used or correlated with our wettability data of fused quartz: the dipole moment values [38-41] the surface tension and its dispersive γ_L^d and polar γ_L^p parts [42-45].

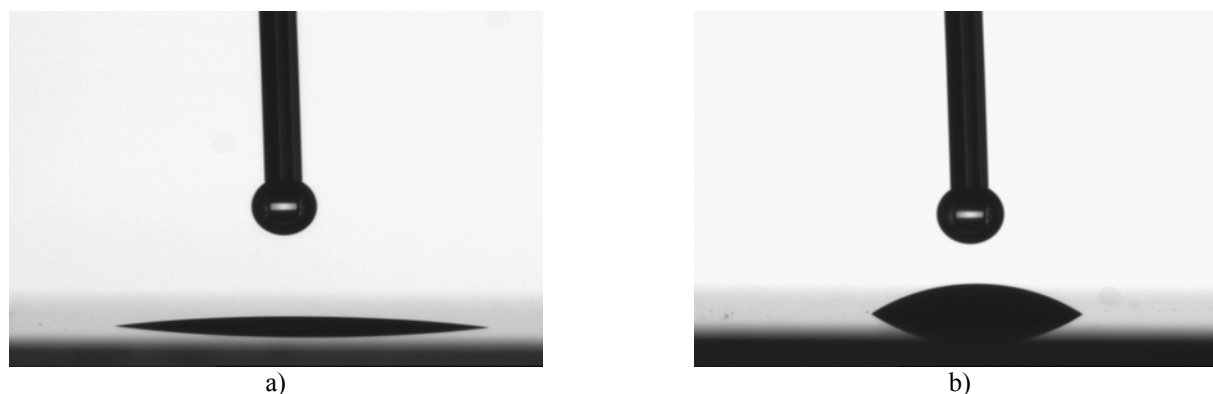


Fig. 4. Water droplets on the plates treated at a) 240°C; b) 1000°C.

Table 1. Contact angle (°) of different liquids on fused quartz treated at two temperatures (°C)

Pretreatment temperature	Water	Glycerol	NP5	Ethylene glycol	Dimethyl sulfoxide
240	5.3	14.2	24.9	8.3	0
1000	33.6	14.8	24	0	6.5

Table 2. Some physical properties of the used probe liquids

Probe liquid	Dipole moment (D)	γ_L (mN/m)	γ_L^d (mN/m)	γ_L^p (mN/m)
Water	1.85	72.8	21.8	51.0
Glycerol	2.56	63.3	33.6	29.7
Ethylene glycol	2.69	48.0	33.8	14.2
Dimethyl sulfoxide	4.11	44.0	36.0	8.0
NP5	1.70	38.1	34.1	4.0

Table 3. Dispersive γ_s^d and polar γ_s^p parts (in mN/m) of surface tension of fused quartz using the indicated calculation methods

Pretreatment temperature (°C)	Owens-Wendt/ least squares		Owens-Wendt/ average		Wu/ least squares	
	γ_s^d	γ_s^p	γ_s^d	γ_s^p	γ_s^d	γ_s^p
240	11.96	61.16	12.36	60.32	23.70	46.67
1000	15.96	46.90	15.96	49.56	25.29	37.48

Starting from these known values of the dispersive and polar parts of the surface tension of the probe liquids and from our experimental results concerning the contact angles, the dispersive and polar parts of the surface tension of the solid (fused quartz) γ_s^d and γ_s^p were estimated either by minimization of the equation system using the least-square method or by solving the equations taken for combinations of two probe liquids. Thus, we have used the eq. (4), which gives a relation among the dispersive and polar parts of the surface tension of the solid substrate, the same quantities for the wetting liquid and also the contact angle that it makes with the substrate. An equivalent of eq. (4) in which the interaction term is expressed as the harmonic mean (eq. (4')) was also applied.

Despite the arguments that the surface pressure cannot be disregarded [46, 47] we have supposed that $\Gamma e_L = 0$ because at the mentioned treatment temperatures and immediately after treatment, during the measurements, there is no liquid film and no water adsorbed on the fused quartz surface. We used this hard approximation (as it was stressed in several works, e.g. in Ref. [48]) due to the experimental difficulties [11] in determining the exact values for materials with very low specific surface area. In addition, we performed the measurements quickly after the treatment was applied to avoid as much as possible the vapor condensation in the measuring room. We have thus obtained values of γ_s^d and γ_s^p (Table 3) from all the

investigated probe liquids. The values γ_S^d and γ_S^p designated as ‘average’ in Table 3, were obtained by averaging the dispersive and polar components of γ_S resulted from solving the eq. (4) for all pairs of liquids that have the condition number of system matrix (as defined by Ref. [49]) low enough. Thus, Della Volpe and Siboni [49] have formulated a numerical criterion to select the test liquids for the determination of the surface free energy of solids (by the method of van Oss, Good and Chaudhury): For a set of more than two test liquids that work offers a way to check the consistency of liquid choice, from the point of view of stability of the numerical procedure of solving the system of equations formed starting from eq. (4) or (4’). The method of Della Volpe-Siboni and the finding of the numerical criterion are beyond the aim of the actual research: However, we retain from this additional check that the choice of liquid pairs in our experiment is consistent from this point of view.

As resulting from Table 3, the thermal treatment at 1000°C leads to the diminution of about 20% of the polar part and the increase of the dispersive part of the surface free energy of fused quartz of about 30%. The same trend of diminution of the polar part is mentioned in literature [6] for fused quartz optically polished.

Figure 5 illustrates the dependence on the contact angle of the surface tension of the probe liquids evaluated using the dispersive and the polar parts from literature, the contact angles from our experiments and eq. (4) as well. The CA determined in our experiments on samples treated at 240°C and 1000°C put the probe liquids in different sequences. For comparison the dependence of the surface tension components of probe liquids are plotted for the same experimental contact angles. These dependences seem to suggest that the polar part might play an important role in the surface tension dependence on the CA, despite to the fact that surface tension seems to be governed by London dispersion forces, which are independent of the permanent dipole moment of the molecules [39].

The surface energy of natural or synthetic quartz and silica films and particles was described by a large range of values between 50 and 230 mN/m and the literature is rich from this point of view [3, 10, 11, 13, 50]. High values as 410-500 mN/m were also obtained by splitting along two different planes of quartz crystal (cited in Ref. [46]). Moreover, dispersive component is mostly smaller than the polar one [50]. All the values obtained by us for γ_S^d , γ_S^p (Table 3) are small in comparison with those found by Staszczuk et al. [4] for fused quartz heated at 250°C, namely $\gamma_S^d = 76$ mN/m and $\gamma_S^p = 115$ mN/m, when the authors used a quite different method (from adsorption isotherm) and took into consideration the pressure of water film. However, high values of γ_S^d , γ_S^p introduced in eq. (4) would lead to perfect wetting for all liquids studied by us, in contradiction with our experimental results and also with those obtained in Ref. [6].

At ca. 250°C a complete desorption of water molecules from the surface occurs; only the silanol and

siloxane groups remain. This surface is completely wetted by water, the contact angle being very low. It seems that heating the surface above this temperature diminishes the number of surface silanol groups by mutual condensation to form siloxane bridges. As a result, the hydrophobicity increases and the contact angle of water also increases [3]. For quartz thermally treated at 1000°C in vacuum, Lamb and Furlong [3] obtain a contact angle of water of 44°. Treating the quartz at 1000°C in atmosphere, we obtained a contact angle of 33.6°, showing that the condensation from silanol groups to siloxane bridges is less complete by heating in atmosphere.

The importance of the surface adsorbed water on the surface tension is put in evidence in the experiments of Janczuk and Zdziennicka [6] which obtained the mean values of $\gamma_S^d = 37.05$ mN/m and $\gamma_S^p = 20.57$ mN/m. These values are also quite different of ours, which are obtained after water desorption from the surface by baking the quartz glass at 240°C.

In comparison with the treatment at 240°C, that at 1000°C produces a diminution of a polar part and an increase of the dispersive part of the surface tension of quartz. The surface is gradually dehydroxylated so that its hydrophilic properties change because siloxane bonds are not of polar nature: the quartz glass surface becomes less hydrophilic. This is in accordance with the findings of Ref. [6] that the surface free energy of quartz results mainly from dispersion and hydrogen-bond intermolecular interactions.

The liquid crystal NP5 behaves atypical among the studied probe molecules since being in the anisotropic (nematic) phase at the measurement temperature it forms non-ideal drops [15]. On the other hand, it is known that the molecular structure of its components includes a big rigid and polar part, containing the benzene rings and the azoxy group. The other part of these molecules is less rigid. How the NP5 molecules interaction with the less polarizable half ionic (after Pauling’s electronegativity scale) Si-O bonds associated to silica surface might be a topic of future research. However, the introduction of NP5 among the probe liquids seemed to be beneficial for the consistency of the obtained results.

We applied the values of quartz surface tension components thus determined to other liquids like either nonpolar (heptane) or polar (formamide). Using the Owens-Wendt approach and the surface tension components from the literature [51] and our values for quartz components, heptane leads to a value too high for the contact angle, namely 39°. At the same time, Wu model leads to contact angle cosine slightly over 1, which can be interpreted as an angle close to zero, or a perfect wettability. From this point of view, this method seems more appropriate than Owens-Wendt one. Formamide yields also to a contact angle cosine slightly over 1, assimilated to a perfect wettability that we found experimentally indeed. These facts seem to indicate that there might be still problems in considering the solid vapor interactions, in particular the spreading pressure.

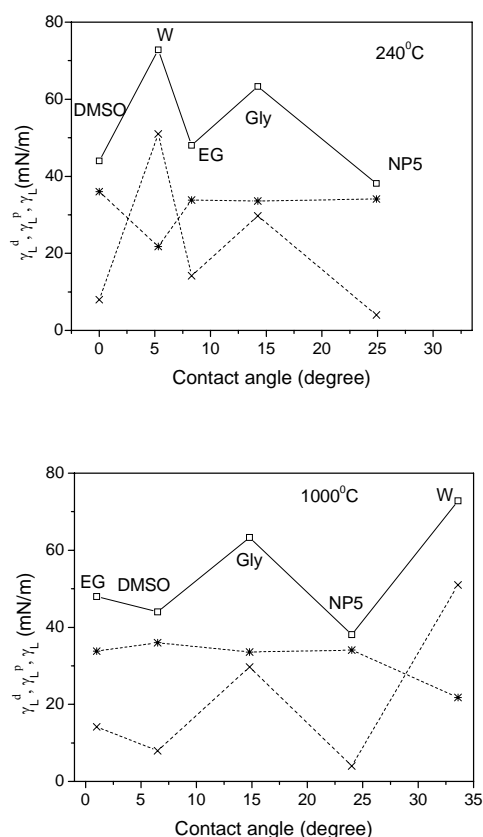


Figure 5. Surface tension (—□—), its dispersive (---x---) and polar (---*---) parts of the probe liquids vs. the contact angle: the first was calculated by eq. (4) and the contact angle observed for the quartz plates treated at the two mentioned temperatures while the latter two parts were taken from literature.

5. Conclusions

The components of surface tension of fused quartz were determined by contact angle measurements of several liquids. The fused quartz plate samples were heated in atmosphere at two temperatures, 240°C and 1000°C to remove water adsorbed on the surface and most of the silanol groups. XPS analysis confirmed this behavior.

Taking from literature the values of the polar and dispersion parts of the liquid surface tension and using the method of geometric mean or the method of harmonic mean for the interaction term, the calculation of the two components for fused quartz give some differences, but their sum do not differ much. Moreover, our tests seem to indicate the method of harmonic mean as better than that of Owens-Wendt.

The polar part of the surface free energy of fused quartz thermally treated is higher than the dispersive part as resulting from both methods (geometrical and harmonic mean). This might be an indication that at the measurement moment, the plate surface was not covered (totally) by the water vapors from the environment.

In agreement with the decrease of the number of silanol groups by the thermal treatment, the polar part of the surface tension shows a decreasing trend by increasing the pretreatment temperature.

The indirect method of contact angle measurements applied for the set of liquids chosen to have complementary interactions with quartz surface, allowed obtaining values for the components of the surface free energy which corroborate with the spectroscopic information concerning the species present on the surface.

Acknowledgements

IZ, VFC, SF and LF acknowledge the financial support of Romanian Ministry of Education and Research under the IDEI 281/2011 project.

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*Corresponding author: irina.zgura@infim.ro ,
lfrunza@infim.ro.