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A study on the components of surface free energy of quartz from contact angle measurements

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Measurements of the contact angle for water, glycerol, formamide, diiodomethane and 1,1,2,2-tetrabromoethane on a quartz surface were made. Using the results obtained, the "geometric mean" approach and long-range and acid–base interaction approach, the dispersion, non-dispersion, Lifshitz–van der Waals and acid–base components of the surface free energy of quartz were determined and compared with those determined in different ways. On the basis of the measurements and calculations it was found that the surface free energy of quartz depends largely on the amounts of silanol groups and physically adsorbed water molecules on its surface. It was also found that the two tested approaches to surface free energy of solids and liquids gave similar results, and it is suggested that the surface free energy of quartz results mainly from dispersion and hydrogen-bond intermolecular interactions.

1. Introduction

Quartz is a high-energy hydrophilic solid being used in many branches of industry. It possesses a high affinity for water [1–4] because on its surface, forces of dispersion and non-dispersion character occur causing strong adsorption of water molecules. As a result a water film is formed in which up to 11–15 statistical monolayers the water molecules possess somewhat different properties compared with those in the bulk phase [1]. The structure of such a film depends on its thickness. It may be expected that the most oriented structure would be found for the first two monolayers on the quartz surface. A monolayer of water molecules on the surface cannot be desorbed by an N_2–H_2 mixture at room temperature [4]. These molecules are so strongly oriented that the structure of the water film is ice-like [2–4]. The monolayer water film can be desorbed by proper thermal treatment. The thermal treatment causes also dehydroxylation of the quartz surface.

Lamb and Furlong [5] showed that at temperatures from 200 to 1000 °C quartz was completely dehydroxylated and its hydrophilic properties changed because of siloxane bond formation. The bond is not of a polar nature and the quartz surface becomes hydrophobic. Changes of silanol group number and physically adsorbed water molecules on the quartz surface depend on the properties of the environment in which it is found. These changes can make the study of quartz wettability and its directly connected surface free energy difficult [2].

A knowledge of quartz surface free energy and its components can be helpful to determine the magnitude of adhesion of water and organic liquids to the quartz surface which, in turn, can be useful to check e.g. flotation processes or the formation of organic coatings on a quartz surface (optical fibre cables).

Thus a main purpose of this paper is to determine quartz surface free energy and its components from contact angle measurements in chosen systems, using different approaches to the surface of solids and liquids and solid–liquid interface free energy.

2. Theory

Thirty years ago Fowkes [6] for the first time divided the surface free energy of solids and liquids into many components due to dispersion interactions, dipole–dipole interactions, dipole–induced-dipole interactions, hydrogen bonding, π-bonding, electrostatic interactions and acceptor–donor interactions. From a practical point of view the surface free energy of solids and liquids can be divided into two components – dispersion (γ^d) and non-dispersion (γ^n). Hence

$$\gamma = \gamma^d + \gamma^n \qquad (1)$$

The dispersion and non-dispersion components of liquid surface tension can be determined among others on the basis of polar liquid–hydrocarbon interfacial tension, assuming that the hydrocarbon surface tension results only from dispersion intermolecular interactions [6]. However, the dispersion and non-dispersion components of solid surface free energy can be determined among others from contact angle measurements in the chosen system. van Oss *et al.* [7] suggest that from the polar liquid–hydrocarbon interfacial tension the dispersion component of the polar liquid cannot be determined, but that the Lifshitz–van der Waals component (γ^{LW}) results from dispersion (γ^d), dipole–dipole type (γ^p) and dipole–induced-dipole

(γ^i) intermolecular interactions. Thus it can be written

$$\gamma^{LW} = \gamma^d + \gamma^p + \gamma^i \qquad (2)$$

van Oss and co-workers [7–10] divide the surface free energy of liquid and solid into Lifshitz–van der Waals and Lewis acid–base components (γ^{AB}). According to their approach [7–10]

$$\gamma = \gamma^{LW} + \gamma^{AB} \qquad (3)$$

The Lewis acid–base component can be expressed as a function of two non-additive parts which can be written in the form

$$\gamma^{AB} = 2(\gamma^+\gamma^-)^{1/2} \qquad (4)$$

where γ^+ is the part of surface free energy of solid and liquid resulting from electron-acceptor intermolecular interactions (Lewis acid) and γ^- is the part resulting from electron-donor interactions (Lewis base).

According to Fowkes' [1] approach extended by Owens and Wendt [11] and Kaelble and co-workers [12, 13], the interface free energy of two phases in contact (phases 1 and 2) can be expressed as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d\gamma_2^d)^{1/2} - 2(\gamma_1^n\gamma_2^n)^{1/2} \qquad (5)$$

Equation 5 expresses the interfacial free energy as a sum of the surface free energy of phases in contact, diminished by a geometric mean of dispersion and non-dispersion interfacial interactions. This approach to interfacial free energy given by Equation 5 is called a geometric mean approach. The approach of van Oss and co-workers [7–10] to interfacial free energy of two phases in contact can also be called a "geometric mean" approach. However, the physicochemical interpretation of the equation describing the interfacial free energy is quite different. This equation is of the form

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^{LW}\gamma_2^{LW})^{1/2} - 2(\gamma_1^+\gamma_2^-)^{1/2} - 2(\gamma_1^-\gamma_2^+)^{1/2} \qquad (6)$$

Using Equations 5 or 6 the Young equation can be solved with respect to the components of solid surface free energy. A general form of the Young equation is

$$\gamma_S - \gamma_{SL} - \Pi e_L = \gamma_L \cos\theta_L \qquad (7)$$

where Πe_L = pressure of liquid film present on the solid surface and θ_L = contact angle. Indices S and L refers to the solid and the liquid, respectively.

Introducing Equation 5 into Equation 7 we obtain

$$\gamma_L \cos\theta_L = -\gamma_L + 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^n\gamma_L^n)^{1/2} - \Pi e_L \qquad (8)$$

Equation 8 can be solved with respect to γ_S^d and γ_S^n by measuring the contact angle for two different liquids on the same solid surface in the four cases: (i) assuming that $\Pi e_L = 0$ for two liquids. (ii) assuming for the first liquid that $\Pi e_L = 0$ and for the second $\Pi e_L = \gamma_S - \gamma_L$, (iii) assuming for the first liquid that $\Pi e_L = \gamma_S - \gamma_L$ and for the second liquid that $\Pi e_L = 0$, and (iv) assuming for both liquids that $\Pi e_L = \gamma_S - \gamma_L$. Then introducing Equation 5 into Equation 7 we obtain [7–10]

$$\gamma_L \cos\theta_L = -\gamma_L + 2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + 2(\gamma_S^+\gamma_L^-)^{1/2} + 2(\gamma_S^-\gamma_L^+)^{1/2} - \Pi e_L \qquad (9)$$

From Equation 9 the γ_S^{LW}, γ_S^+ and γ_S^- components of solid surface free energy can be determined on the basis of contact angle measurements for three different liquids on the same solid surface.

For calculations of γ_S^{LW}, γ^+ and γ^- it is commonly assumed that $\Pi e_L = 0$ [7–10]. Equation 9 can also be solved in the case when for one or all liquids the assumption that $\Pi e_L = \gamma_S - \gamma_L$ holds. Hence, in theory there are eight possible solutions of Equation 9 with respect to γ_S^d, γ_S^+ and γ_S^-.

3. Experimental procedure

Measurements of the contact angle on quartz plates were made by the sessile drop method using a microscope–goniometer system at 25 × magnification.

The quartz plates (10 mm × 10 mm) used for measurements were from a quartz glass cell. Before the measurements the plates were boiled three times in hydrochloric acid (1 : 1), then in doubly distilled water and washed in a water ultrasonic bath for 20 min. Next they were heated at 105 °C for 1 h and placed in a desiccator filled with molecular sieves (0.4 nm + 0.5 nm). After cooling to room temperature (20 °C in a thermostatted room) the quartz plate was placed in a measuring chamber in which the relative humidity was ca. 60% for 24 h. After this time a liquid drop of 2 mm^3 was settled on the quartz plate and immediately the contact angle was read out several times on the left and right sides of the drop.

Measurements were made at the temperature 20 ± 0.1 °C with an accuracy ± 1° and the standard deviation did not exceed ± 1.5. Using the above-mentioned procedure, contact angle measurements for water, glycerol, formamide, diiodomethane and 1,1,2,2-tetrabromoethane on at least ten quartz plates were made.

4. Results and calculations

The results obtained for contact angles with water (θ_W), glycerol (θ_G), formamide (θ_F), diiodomethane (θ_D) and 1,1,2,2-tetrabromoethane (θ_T) on the quartz surface are presented in Table I. It appears that the highest value of contact angle is observed for θ_D and the lowest for θ_F. It is interesting to note that the values of contact angle for water and glycerol are almost the same.

On the basis of the values of contact angle listed in Table I the dispersion and non-dispersion of Lifshitz–van der Waals and Lewis acid–base components of quartz surface free energy can be determined. Introducing into Equation 8 the literature values ([14–17], Table II) of dispersion and non-dispersion

TABLE I Measured values of contact angle on quartz

	Parameter				
	θ_W	θ_G	θ_F	θ_D	θ_T
Contact angle (deg)	26.8	26.1	13.4	36.5	18.9

TABLE II Values of the dispersion (γ_L^d) and non-dispersion (γ_L^n) components of liquid surface tension taken from the literature [14–17]

Liquid	γ_L^d(mN m^{-1})	γ_L^n(mN m^{-1})	γ_L(mN m^{-1})
Water	21.80	51.00	72.80
Glycerol	33.60	29.70	63.30
Formamide	31.39	27.01	58.4
Diiodomethane	50.42	0.38	50.8
1,1,2,2-tetra-bromoethane	47.92	1.78	49.70

components of liquid surface tension for water, glycerol, formamide, diiodomethane and 1,1,2,2-tetrabromoethane and values of the contact angle for these liquids, the dispersion and non-dispersion components of quartz surface free energy were calculated. For calculations the values of the contact angle for a liquid pair including one polar and one apolar liquid (water–diiodomethane, water–1,1,2,2-tetrabromoethane, glycerol–diiodomethane, glycerol–1,1,2,2-tetrabromoethane, formamide–diiodomethane and formamide–1,1,2,2-tetrabromoethane) were used.

For all possible pairs of liquids it was assumed that in Equation 8 $\Pi e_L = 0$ (see Table III, superscript b). In addition, in the case of the liquid pairs of water–diiodomethane and water–1,1,2,2-tetrabromoethane, calculations were also made of γ_S^d and γ_S^n for quartz, assuming that for water $\Pi e_W = \gamma_S - \gamma_W$ and for diiodomethane or 1,1,2,2-tetrabromoethane $\Pi e_O = 0$ (see Table III, superscript c, Πe_O-organic liquid film pressure). All values of γ_S^d and γ_S^n calculated from Equation 8 are presented in Table III.

This Table also presents the values of quartz surface free energy components calculated from the contact angles for liquid pairs including water. From Table III it can be seen that γ_S^d and γ_S^n values calculated from the contact angles for organic liquids are close to each other; however, using θ_W and θ_D or θ_W and θ_T values for calculations in Equation 8, the γ_S^d values are slightly lower and γ_S^n higher (by ca. 10 mJ m^{-2}) than those calculated from the contact angles for organic liquids.

TABLE III Values of the dispersion (γ_S^d) and non-dispersion (γ_S^n) components of quartz surface free energy (γ_S) calculated from Equation 8

Liquid pair[a]	γ_S^d(mJ m^{-2})	γ_S^n(mJ m^{-2})	γ_S(mJ m^{-2})
1–4[b]	35.44	33.11	68.55
1–5[b]	34.40	33.78	68.18
1–4[c]	36.59	22.15	58.74
	31.40	95.59	126.99
1–5[c]	36.91	22.32	59.23
	25.77	98.17	123.94
Average	36.75	22.24	59.99
	28.59	96.88	125.47
2–4	36.66	21.00	57.66
3–4	36.69	20.74	57.43
2–5	37.39	20.42	57.81
3–5	37.49	20.11	57.59
Average	37.06	20.57	57.63

[a] (1) Water, (2) glycerol, (3) formamide, (4) diiodomethane, (5) 1,1,2,2-tetrabromoethane.

[b] γ_S^d and γ_S^n values calculated assuming that $\Pi e_W = 0$ and $\Pi e_O = 0$ (O = organic liquid).

[c] γ_S^d and γ_S^n values calculated assuming that $\Pi e_W = \gamma_S - \gamma_W$ and $\Pi e_O = 0$.

Assuming for calculations that $\Pi e_W = \gamma_S - \gamma_W$ and $\Pi e_O = 0$, two values for γ_S^d and γ_S^n are obtained from contact angles for each pair of liquids (water–diiodomethane, water–1,1,2,2-tetrabromoethane). It is interesting to note that one of the value pairs of γ_S^d and γ_S^n is almost the same as that calculated assuming that the pressure of the film for each of two organic liquids taken into consideration on the quartz surface is equal to zero.

Assuming that for each tested liquid $\Pi e_L = 0$, the values of Lifshitz–van der Waals and Lewis acid-base components of quartz surface free energy can be calculated. To calculate the above-mentioned components the values of contact angle measured for three different liquids must be taken into consideration. For calculations, the values of contact angle for such three liquids of which one was apolar and two polar or one polar and two apolar were chosen. The γ_L^{LW}, γ_L^+ and γ_L^- values used for calculations were taken from the literature [9, 17] (Table IV).

In the case of three liquids including water, calculations both for $\Pi e_W = 0$ and $\Pi e_W = \gamma_S - \gamma_W$ were made. All calculated values of Lifshitz–van der Waals (γ_S^{LW}), electron-acceptor (γ_S^+) and electron-donor (γ_S^-) components are presented in Table V. The table also gives the values of γ_S^{AB} and γ_S for quartz. The values of the acid–base component (γ_S^{AB}) of quartz surface free energy (γ_S) were calculated from Equation 4; then $\gamma_S = \gamma_S^{LW} + \gamma_S^{AB}$ (see Equation 3).

TABLE IV Values of the Lifshitz–van der Waals (γ_L^{LW}), electron-acceptor (γ_L^+), electron-donor (γ_L^-) and acid–base (γ_L^{AB}) components of liquid surface tension taken from the literature [9–17]

Liquid	γ_L^{LW} (mN m^{-1})	γ_L^+ (mN m^{-1})	γ_L^- (mN m^{-1})	γ_L^{AB} (mN m^{-1})	γ_L^{Tot} (mN m^{-1})
Water	21.8	25.5	25.5	51.0	72.8
Glycerol	33.6	9.89	22.3	29.7	63.3
Formamide	31.39	10.52	17.34	27.01	58.4
Diiodomethane	50.8	0.72	0.0	0.0	50.8
1,1,2,2-tetra-bromoethane	49.7	3.13	0.0	0.0	49.7

TABLE V Values of the Lifshitz–van der Waals (γ_S^{LW}), Lewis acid (γ_S^+) and Lewis base (γ_S^-) components of quartz surface free energy calculated from Equation 9

Liquids	γ_S^{LW} (mJ m^{-2})	γ_S^+ (mJ m^{-2})	γ_S^- (mJ m^{-2})	γ_S^{AB} (mJ m^{-2})	γ_S (mJ m^{-2})
1–4–5[b]	36.47	22.92	10.70	31.32	67.79
1–4–5[c]	36.47	11.42	10.70	22.11	58.58
2–4–5	36.47	9.80	10.70	20.48	56.95
3–4–5	36.47	9.99	10.70	20.68	57.15
2–3–4	36.03	8.82	12.80	21.25	57.28
2–3–5	35.36	8.99	13.25	21.83	57.19
Average	36.08	9.40	11.86	21.12	57.20

[b,c] See Table III description.

It follows from Table V that γ_S^{LW} values calculated from contact angles for different sets of three liquids are almost the same. These values are higher than γ_S^{AB} ones. Using for calculation only the contact angle values for sets of organic liquids, γ_S^+ values lower than γ_S^- are obtained. γ_S^{AB} values calculated from contact angle values for sets of three liquids including water assuming that $\Pi e_W = 0$ and $\Pi e_O = 0$ are ca. $10\ \mathrm{mJ\,m^{-2}}$ higher that those calculated from only organic liquid contact angles, and $\gamma_S^+ > \gamma_S^-$. Comparing the average values of γ_S^{LW} and γ_S^{AB} with γ_S^d and γ_S^n, respectively (Tables III and IV) it can be stated that they are close to each other.

5. Discussion

A study on wettability of quartz surface carried out earlier [2] indicates that the values of the contact angle in the system quartz–water-drop–air depend on the contacting time of the "clean" quartz surface with water molecules and on the relative humidity of the air. Measuring the contact angle for water drops settled on the quartz surface after different times of quartz plate residence in the measuring chamber filled with saturated water vapour, an increase of contact angle value was observed from 0 to 52° [2].

A long time of contact of quartz plates with water vapour caused a decrease in contact angle from 52 to 24°. However, measurements of the contact angle for quartz plates in contact with air at different relative humidities indicated an increase in contact angle values as a function of relative humidity [18]. Taking into account the influence of the contacting time of quartz with water molecules and the presence of water vapour in our studies, the conditions which allow for determination of quartz surface properties in a natural environment (long time of quartz surface contacting with water molecules and high relative humidity) were established. The contact angle value measured for water (26.8°) differed only slightly from that measured earlier for a quartz plate in contact with water vapour for 24 h at 20 °C (24°) [2]. However, the θ_D value (36.5°) is almost the same as that measured by Bernett and Zisman [18] in air at a relative humidity of 95% (37°).

Taking into account the great changes of quartz wettability by water and organic liquids depending on the condition of its contact with water molecules, the question of the reason for this phenomenon can be raised. Of course, the change of values of quartz surface free energy components results from the influence of water molecule adsorption on the quartz surface. The investigations made earlier indicate that the value of the dispersion component of quartz surface free energy heated to 250 °C is equal to $76\ \mathrm{mJ\,m^{-2}}$; however, the non-dispersion component is ca. $115\ \mathrm{mJ\,m^{-2}}$ [4]. The surface of such quartz is completely wetted by water [4].

One should take into account that at 250 °C a complete desorption of water molecules from the quartz surface occurs; only the silanol and siloxane groups remain [5] and the density of silanol groups reaches its maximum. Lamb and Furlong [5] on the basis of their investigations indicate that on heating quartz in a vacuum in the range of temperature from 200 to 1000 °C, an increase of the contact angle value for water on its surface is observed from 0 to 44°. They explained this fact by gradual dehydroxylation of the quartz surface which in consequence leads to the conversion of silanol groups into siloxane ones. As shown by numerous chromatographic investigations, siloxane groups do not interact by hydrogen bonding with the adherent medium [19, 20]. Hence it is possible that on heating quartz in the range of temperature from 200 to 1000 °C a decrease of the non-dispersion component from 115 to zero occurs.

Assuming that the value of contact angle for water equal to 44° [4] corresponds to a quartz surface for which $\gamma_S^n = 0$, the dispersion component of quartz surface free energy can be calculated from Equation 8 in the two cases: for $\Pi e_W = 0$ and for $\Pi e_W = \gamma_S - \gamma_W$. The value calculated from Equation 8 assuming that $\Pi e_W = 0$ is equal to $179.7\ \mathrm{mJ\,m^{-2}}$. Assuming that $\Pi e_W = \gamma_S - \gamma_W$, Equation 8 cannot be solved.

On heating quartz in the range of temperature from 200 to 1000 °C, the dispersion component of its surface free energy increases from 76 to $179.2\ \mathrm{mJ\,m^{-2}}$. It is interesting to note that under the influence of temperature the total surface free energy of quartz changes only slightly from 191 to $179.1\ \mathrm{mJ\,m^{-2}}$.

On placing quartz in a medium in which water vapour is present the silanol groups tend to be hydrated, and therefore strong physical adsorption of water molecules occurs [2, 20]. As a result of this, a water film is formed in which the water molecules are strongly oriented and a water drop settling on the surface does not spread completely. In the system quartz–water-drop–air the water drop does not come into contact with a "clean" surface of quartz but with the quartz surface covered with a water film.

Fowkes [1], summing up all dispersion interactions of "potential pairs" among all elements of the bulk phase on the surface and all elements of the bulk phase under the surface, found a way of calculating the dispersion component of surface free energy of quartz covered with a water film. Using the adsorption data for water on a quartz surface, Fowkes calculated the dispersion component of its surface free energy with a monolayer water film as equal to $29.7\ \mathrm{mJ\,m^{-2}}$. Taking into account this value and changes of water film pressure as a function of its thickness, the non-dispersion component of surface free energy of quartz covered with a monolayer water film was also determined by Jańczuk [21]. The value of this component is equal to $91.3\ \mathrm{mJ\,m^{-2}}$. The γ_S^d and γ_S^n values of a quartz surface with a monolayer water film determined in this way differ only slightly from those calculated in this paper (Table III) from Equation 8 assuming that $\Pi e_W = \gamma_S - \gamma_W$ and $\Pi e_O = 0$. However, using the values of $\gamma_S^d = 29.7$ and $\gamma_S^n = 91.3\ \mathrm{mJ\,m^{-2}}$ [1, 2] in Equation 8, the values of θ_L calculated for glycerol and formamide strongly differ from those measured independent of the assumptions made for Πe_L.

This shows that different values of quartz surface free energy probably decide the wettability of quartz by these liquids. The question can be raised why the γ_S^d and γ_S^n values equal to 37.06 and 20.57 mJ m^{-2}, respectively (Table III) determine the wettability of quartz by organic liquids assuming that $\Pi e_L = 0$. Some investigators treat the film pressure on the solid surface as a sum $\Pi e_L^d + \Pi e_L^n$ [22] where Πe_L^d results from dispersion and Πe_L^n from non-dispersion intermolecular interactions. Taking into account this fact, the spreading film pressure can be expressed by the equation

$$\Pi e_L(s) = 2(\gamma_S^d \gamma_L^d)^{1/2} - 2\gamma_L^d + 2(\gamma_S^n \gamma_L^n)^{1/2} - 2\gamma_L^n \qquad (10)$$

Assuming that on the quartz surface as a result of its contact with water vapour a water film is formed, the pressure of which is equal to $\Pi e(s)$, the γ_S^d and γ_S^n values for quartz covered with a water film can be calculated. Introducing into Equation 10 the values of $\gamma_S^d = 76, \gamma_S^n = 115, \gamma_W^d = 21.8$ and $\gamma_W^n = 51$ mJ m^{-2} [6] the $\Pi e_W^d(s)$ and $\Pi e_W^n(s)$ values were calculated as 37.77 and 51.17 mJ m^{-2}, respectively. Subtracting $\Pi e_W^d(s)$ from γ_S^d and Πe_W^n from γ_S^n we obtain 38.23 and 63.83 mJ m^{-2}, respectively. The value 38.23 mJ m^{-2} differs only slightly from the γ_S^d value calculated from contact angles for organic liquids assuming that $\Pi e_L = 0$ (37.06 mJ m^{-2}, see Table III). However, the value of 63.88 mJ m^{-2} is three times higher than γ_S^n. Hence it may be stated that in the case of strong orientation of water molecules on the quartz surface, the decrease of the non-dispersion component of quartz surface free energy is higher than that resulting from Equation 10; the system quartz/water film–water drop–air is not comparable to that of quartz/water film–organic liquid drop–air.

The non-dispersion component of quartz surface and water tension results first of all from acid–base intermolecular interactions which are strongly oriented with respect to the contacting surface, contrary to long-range dispersion forces. Water molecules contacting the quartz surface directly are strongly oriented. The orientation of these molecules must occur as a result of the decrease of quartz surface free energy. In consequence, a significant decrease of the interactions of the quartz/water film surface with the adherent medium takes place.

If we assume that there exists a possibility of increasing and not only decreasing the solid surface free energy by a liquid film, then the value of θ_W on the quartz surface can be explained on the basis of the components of its surface free energy calculated from contact angles for organic liquids assuming that $\Pi e_L = 0$. Assuming that a water film derived from a water drop settled on the quartz surface increases its surface free energy up to the value of water surface tension, the contact angle θ_W calculated from Equation 8 using $\gamma_S^d = 37.06$ and $\gamma_S^n = 20.57$ is equal to 28.5° and is a little higher than the measured one (26.8°). However, this fact does not give enough evidence that on the basis of the components of quartz surface free energy determined from contact angles for organic liquids the wettability of its surface by water can be predicted.

Knowledge of only dispersion and non-dispersion components of solid surface free energy does not provide complete explanations of the solid and liquid interactions. Recently the approach of van Oss *et al.* [7–10] for determination of solid surface free energy has been often used. As can be seen from comparing the data listed in Tables III and V, the dispersion and Lifshitz–van der Waals components are similar (37.06 and 36.09 mJ m^{-2}). This proves that contributions of dipole–dipole and dipole–induced-dipole intermolecular interactions to the quartz surface free energy are small. In turn, the non-dispersion component is close to the Lewis acid–base component of quartz surface free energy, which also confirms the above-mentioned conclusion. The similar values of γ_S^d and γ_S^{LW} or γ_S^n and γ_S^{AB} indicate that the two approaches to solid and liquid surface free energy give similar results.

According to Equation 4 the γ_S^{AB} component depends on the two parts of surface free energy γ_S^+ and γ_S^-. The values of γ_S^+ calculated from θ_L for organic liquids alone are lower than γ_S^-; however, when calculated from θ_L including also water, the values of γ_S^+ are higher than those of γ_S^-. This could indicate that the surface free energy of quartz covered with a water film under the water drop is different from that under an organic liquid drop. On the other hand the components of a strongly hydrated solid surface free energy determined from contact angle measurements for organic liquids cannot predict fully the wettability of the solid by water.

6. Conclusions

The surface free energy of quartz depends to a great extent on the number of silanol groups and physically adsorbed molecules of water on its surface. The components of quartz surface free energy determined from contact angle measurements for organic liquids on its surface differ from those determined from contact angles for liquids including water. The dispersion component differs only slightly from the Lifshitz–van der Waals component, which points to a small contribution of dipole–dipole and induced-dipole–dipole intermolecular interactions to the quartz surface free energy. Two approaches to interfacial free energy, e.g. that of Fowkes and other authors and that of van Oss *et al.*, give similar results; however, the approach of van Oss *et al.* provides more information about the influence of different kinds of intermolecular interaction on the surface free energy of quartz.

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