Time dependence wettability of quartz with water

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Contact angles as a function of time were measured in two systems: "dry" quartz glass plate—water droplet—saturated water vapour and wetted in excess with water quartz plate—water droplet—air "dried" with molecular sieve. In both the cases contact angles increased from zero to 52°—54° in the period of time equal to 30 min. However, if the "dry" plate was exposed to the water vapour for 24 h the contact angle decreased to 24°. To explain the observed contact angles models of the interfaces of the quartz—water—air system were proposed. Using GGFY equations contact angles were calculated as a function of the water film decrease of surface density of Gibbs energy of quartz behind and under a water droplet. The experimental values of the contact angle fit into the calculated ranges of the contact angle changes.

Были измерены краевые углы в зависимости от времени в двух системах: «сухая» пластинка из кварцевого стекла—капля воды— —насыщенный водяной пар и в избытке воды смоченная кварцевая пластинка—капля воды—воздух «высушенный» молекулярным ситом. В обоих случаях контактные углы возросли с нуля до 52°—54° в течение времени равным 30-ти минутам. Однако, если «сухая» пластинка была подвержена действию водяного пара в течение 24 часов, краевой угол понизился до 24°. Для объяснения наблюденных краевых углов были предложены модели граничной поверхности системы кварц—вода— —воздух. Применением уравнений GGFY были вычислены краевые углы в качестве функции понижения водяной пленкой поверхностной плотности Гиббсовой энергии кварца за и под каплей воды. Экспериментальные данные контактного угла находятся в расчитанных пределах изменений контактного угла.

Possibility of spreading of a liquid on a solid surface can be determined by the spreading coefficient [1, 2]. This coefficient is equal to the difference between work of the solid—liquid adhesion and the work of cohesion of the liquid [1, 2]. Moreover, it is also equal to the work of spreading [3, 4]. From the above it results that a liquid will completely wet a solid if surface density of Gibbs energy (γ_i) of the solid (γ_S) is higher than the sum of the solid—liquid interfacial density of Gibbs energy ($\gamma_{S/L}$) and γ_L of the liquid. On the other hand, water drop settled on a solid surface would spread over the surface in two stages [5]. In the first, a water film

forms on the solid surface as a result of water vapour adsorption or water molecules diffusion from the drop. Thickness of the film depends on nature of the solid and the liquid.

The second stage is the actual spreading process. The film formation occurs at the cost of γ_s [1, 2, 6], which can be decreased to such a level that, despite of theoretical circumstances of complete wetting of the solid, the liquid drop forms a finite contact angle. Such a situation can appear in the case of quartz during wetting it with water. The value of γ_Q [7] is much higher than the sum of the values of $\gamma_{O/w}$ and γ_w.

So, water should wet completely the quartz surface. On the other hand, surface properties of quartz depend to a high degree on thermal pretreatment and contact time of quartz with water [8—13].

Lamb and *Furlong* [14] have shown that contact angle value of water drop on quartz surface changed with temperature of the quartz preheating. Molecules of water in the film even up to eleven statistical monolayers possess somewhat different energy in comparison with those in the bulk phase [8]. However, structure of such film depends on its thickness. It may be expected that the most ordered structure would be found for the first two monolayers from the quartz surface. A monolayer of water molecules on the surface cannot be desorbed by N_2—H_2 mixture at room temperature [7]. Of course, the water film decreases polar and dispersion parts of γ_Q [8, 10] and these decreasings depend on thickness (the density of film volume V_f/A), structure, and time of water contact with quartz [10].

Therefore, theoretical circumstances show that it may be expected that γ_Q can be decreased sufficiently by a water film to be lower than the sum of $\gamma_{O/w}$ and γ_w.

If it were real, a finite contact angle of water drop on the quartz surface could be expected. To find out if such situation is possible contact angle was measured as a function of time for a water droplet settled on the "dry" quartz surface in saturated water vapour, and in the second series of the experiments, for a water droplet settled on quartz surface previously wetted in excess with water.

Experimental

Contact angles were measured by sessile drop method with a telescope-goniometer system at a magnification of 25 times.

For the measurements the quartz glass plates 1 cm × 1 cm were used, which were boiled triply in HCl solution (volume ratio = 1 : 1), rinsed several times with distilled water and then boiled triply in doubly distilled water. After that, the quartz plates were heated at 250 °C for 1 h and placed into desiccator with 4—5 × 10^{-10} m molecular sieve. After cooling to *ca.* 20 °C they were placed in the measurement box, thermostated at $\theta = (20.0 \pm 0.1)$ °C and contact angle of a water drop (2 mm^3 of volume) was measured.

In the first series, inside the box saturated water vapour was present, because a vessel with water was placed there for 24 h before.

However, in the second series of the experiments, where the quartz plates were wetted with water in excess (dipped into water for a moment) in the measured box the molecular sieve 4—5 10^{-10} m was placed, which at equilibrium ensured the vapour pressure *ca.* 1×10^{-3} Pa.

In the first series contact angle of water drop on "dry" quartz surface was measured immediately after the drop settling, then, after 0.5 min, 5.5 min, 10.5 min, 18 min, and 30 min and after 24 h, each time for a new water drop and after "cleaning procedure" of the plate.

In the second series, water drop was settled on the "wet" quartz plate after desired time was over from the moment when the plate was placed in the box, namely after 2 min, 4 min, 8 min, 15 min, and 30 min. Similarly as above the cleaning procedure was repeated after each measurement.

Results and discussion

The values of determined contact angle are listed in Table 1. It can be seen there that in both series contact angle increases as a function of time reaching a maximum. This maximum value (52° and 54°, respectively) is obtained after 30 min from the moment of placing the quartz plates in the measurement box. However, if "dry" quartz plate was allowed to be in contact with saturated water vapour for 24 h in the box the contact angle value decreased to 24°.

Table 1

Experimental values of water drop contact angle on "dry" quartz plate in saturated water vapour and on "wet" quartz plate in dried air (molecular sieve 4×10^{-10} m $+ 5 \times 10^{-10}$ m) as a function of time

"Dry" quartz plate		"Wet" quartz plate	
Time min	Contact angle/°	Time min	Contact angle/°
0.5	11	2	0
5.5	19	4	26
10.5	34	8	39
18	40	15	45.5
30	52	30	54
24 h	24		

The changes of contact angle values may be connected with changes in γ_Q caused by a water film formed around the droplet, and also, by changes in the water film structure under the water droplet during the time of contact.

To find any explanation for this phenomenon let us consider the Young equation to which term describing the water film pressure under and around the droplet is introduced [1, 2]. Thus the modified equation reads

$$\gamma_Q - \Pi_{(I,II)} - \gamma_{(Q,I)/w} = \gamma_w \cos \Theta \qquad (1)$$

where $\gamma_{(Q,I)/w}$ is the interfacial density of Gibbs energy of quartz water film I in contact with water, Θ is the contact angle measured through the water phase, $\Pi_{(I,II)}$ is the decrease in γ_Q behind the water droplet.

In our previous paper [15] it was suggested that the value of the reduction of γ_Q under the water droplet (Π_I) for a polar liquid could possibly be treated as that resulting additively from polar and dispersion interactions. Hence, it can be written that $\Pi_I = \Pi_I(d) + \Pi_I(p)$ where $\Pi_I(d)$ and $\Pi_I(p)$ is the reduction caused by dispersion and polar component, respectively, and Π_I is the film surface density of Gibbs energy.

If we assume that $\Pi_{(I,II)}$ in eqn (1) is equal to the sum of $\Pi_I + \Pi_{II}$, and taking into account the above assumption, the following expression may be obtained

$$\gamma_{(Q,I)/w} = \gamma_Q - \Pi_I + \gamma_w - 2\sqrt{(\gamma_Q(d) - \Pi_I(d))\gamma_w(d)} -$$
$$- 2\sqrt{(\gamma_Q(p) - \Pi_I(p))\gamma_w(p)} \qquad (1a)$$

and then, according to the GGFY theory [6] eqn (1) reads

$$\gamma_w \cos \Theta = -\gamma_w + 2\sqrt{(\gamma_Q(d) - \Pi_I(d))\gamma_w(d)} +$$
$$+ 2\sqrt{(\gamma_Q(p) - \Pi_I(p))\gamma_w(p)} - \Pi_{II} \qquad (2)$$

where $\gamma_Q(d)$ and $\gamma_Q(p)$ is dispersion and polar component of γ_Q, respectively, $\gamma_w(d)$ and $\gamma_w(p)$ is the dispersion and polar component of γ_w, and Π_{II} is a part of the value of $\Pi_{(I,II)}$ resulting from the difference between $\Pi_{(I,II)}$ and Π_I.

From eqn (2) it is possible to calculate contact angle value in quartz—water drop—air system for two cases. First, (see schematic representation in Fig. 1a) when the three-phase contact line is situated on the bare surface of quartz and $\Pi_I = 0$, and the second, when this line is in some distance h from the bare surface of quartz, i.e. a few monolayers of water molecules, when $\Pi_I > 0$ (Fig. 1b).

It seems possible that the first case may reflect the conditions when "dry" quartz plate was placed in the measurement box containing saturated water vapour, and the second would correspond to the system of quartz plate wetted in excess with water and then placed in the box with molecular sieve.

If $\Pi_I = 0$, then obviously $\Pi_I(d) = 0$ and $\Pi_{II}(p) = 0$, and in eqn (2) the only unknown independent variable is $\Pi_{II} = \Pi_{(I,II)}$. In this case from eqn (1) results that in the range of $\Pi_{(I,II)}$ from 0 to 89 mJ m^{-2} ($\gamma_Q - \Pi_{(I,II)} > \gamma_{Q/w} + \gamma_w$) contact angle value is impossible to be greater than zero, if $\gamma_Q = 191$ mJ m^{-2}, $\gamma_{Q/w} = 29.2$ mJ m^{-2}, $\gamma_w = 72.8$ mJ m^{-2} [6, 7].
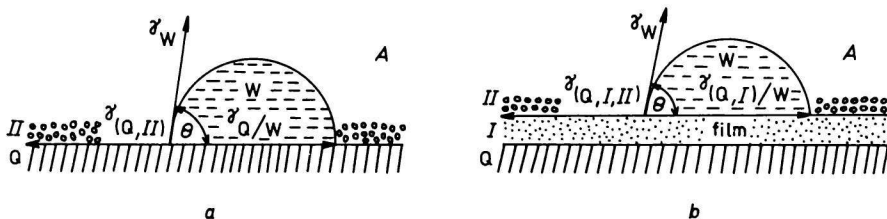

Fig. 1. Schematic representation of quartz—water drop—air system for: a) a water film presence behind the drop ("dry" quartz plate in saturated water vapour); b) a water film presence behind and under the water drop ("wet" quartz plate in dried air).

For $\Pi_{(I,II)} > 89$ mJ m^{-2}, a water drop settled on the quartz surface covered with the water film would not spread. This $\Pi_{I,II}$ value is equal to the work of spreading, W_s, for water on quartz and it corresponds to zero value of contact angle in the system. During the water vapour adsorption process on the quartz surface its surface free energy decreases until it reaches the value equal to $\gamma_w = \gamma_Q - \Pi_{(I,II)}$ [10]. Therefore, the maximum value of the film pressure could be equal: $\Pi_{max} = (191 - 72.8)$ mJ m^{-2} = 118.2 mJ m^{-2}, and theoretically, for the first discussed case (Fig. 1a) possible range of contact angle Θ values calculated from eqn (2), for 89 mJ m$^{-2} < \Pi_{(I,II)} < 118.2$ mJ m^{-2} lies between 0° and 53.2°.

Thus calculated values are plotted in Fig. 2A as a function of Π_{II}. To calculate the above contact angles the following values were used: $\gamma_Q(d) = 76$ mJ m^{-2} [6], $\gamma_Q(p) = 115$ mJ m^{-2} [7], $\gamma_w = 72.8$ mJ m^{-2}, $\gamma_w(d) = 21.8$ mJ m^{-2}, $\gamma_w(p) = 51$ mJ m^{-2} [6]. From Fig. 2a and Table 1 it can be seen that maximum values of contact angle calculated (eqn (2)) and measured after 30 min in both systems are very similar, 53.2°, 52°, and 54°, respectively. Moreover, the measured values of contact angle for the first system ("dry" quartz plate) may be fitted into the calculated ones (Fig. 2a). This would support the model that in this case the three-phase contact line is on the bare quartz surface, and around the water drop water film is present which causes decreasing of γ_Q down to the value of γ_w.

However, this model does not explain the changes of contact angle in the system when the quartz plate was wetted in excess with water, and then "dried" in the measurement box by molecular sieve. It may be concluded that in this case Π_I value

cannot be equated to zero in eqn (2), so a new model should be recognized. Such a model is presented in Fig. 1b. Several different values for Π_I and Π_{II} describing the changes of Θ seem to be possible [15]. However, the situation where $\Pi_I + \Pi_{II} = \gamma_Q - \gamma_w$, and Π_I changes from 0 to $\gamma_Q - \gamma_w = 118.2$ mJ m^{-2} seems very preferable. Clearly, for $\Pi_I = 0$ and $\Pi_{II} = $ max, the contact angle value reaches 53.2° and it corresponds to the first system ("dry" plate) at the moment of maximum contact angle (Fig. 2a and 2b).
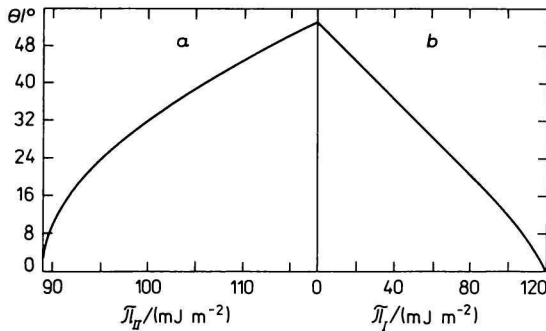

Fig. 2. Calculated contact angles in the system quartz—water drop—air as a function of the water film decrease in γ_Q: a) for the water film decrease γ_Q behind the drop, Π_{II}; b) for the water film decrease in γ_Q under the drop, Π_I, and for the condition that

$$\Pi_I + \Pi_{II} = 118.2 \text{ mJ m}^{-2} = \Pi_{(I, II)}.$$

To calculate contact angle values from eqn (2), $\Pi_I > 0$, the $\Pi_I(d)$ and $\Pi_I(p)$ values, resulting from particular Π_I values, must be known. In our previous paper [15] it was suggested that the decrease in the solid surface density of Q resulting from the presence of liquid film may be described by the relation

$$\Pi_{(I, II)} = 2\sqrt{\gamma_S(d)\gamma_L(d)} + 2\sqrt{\gamma_S(p)\gamma_L(p)} - \gamma_L(1 + \cos\Theta) \quad (3)$$

where $\gamma_S(d)$ and $\gamma_S(p)$ is the dispersion and polar component, respectively, of γ_S, $\gamma_L(d)$, $\gamma_L(p)$ is the dispersion and polar component, respectively, of γ_L.

If one recognizes that eqn (3) is valid for every thickness (specific volume) of the water film on quartz surface, and denoting $1 + \cos\Theta = x$, $\Pi_{(I, II)} = \Pi_I$, this equation reads

$$\Pi_I = 2\sqrt{\gamma_Q(d)\gamma_w(d)} + 2\sqrt{\gamma_Q(p)\gamma_w(p)} - x\gamma_w \quad (4)$$

Then

$$\Pi_I(d) = 2\sqrt{\gamma_Q(d)\gamma_w(d)} - x\gamma_w(d) \quad (5)$$

and

$$\Pi_I(p) = 2 \sqrt{\gamma_Q(p)\gamma_w(p)} - x\gamma_w(p) \tag{6}$$

From the set of the last three equations one can determine $\Pi_I(d)$ and $\Pi_I(p)$ for particular value of Π_I. Thus calculated values of the $\Pi_{(I,II)}$ were then used for the contact angles calculations from eqn (2) using Π_I values from 0 to 118.2 mJ m^{-2} and $\Pi_{II} = 118.2$ mJ m$^{-2} - \Pi_I$. The calculated contact angles are presented in Fig. 2B as a function of Π_I. As it can be seen calculated contact angles decrease for increasing Π_I values (increasing the water film thickness) and for Π_I tending to 118.2 mJ m^{-2} the angles approach to zero value. This value of Π_I corresponds to the value of $\gamma_{(Q,I)/w}$. The contact angles measured on the "wet" quartz plate (Table 1) fit in the calculated range of the contact angle values (Fig. 2b).

It is very interesting that contact angle measured on "dry" quartz plate after 24 h equal to 24° (Table 1), corresponds to $\Pi_I = 70$ mJ m^{-2}, if one calculates the angle from eqn (2). This value of Π_I results from one statistical monolayer of water adsorbed on quartz surface [7]. It would suggest that for a long time of water contact with quartz a fixed structure of at least monolayer water film is formed.

So, the above models seem to explain the measured changes in the contact angle of a water drop on "dry" quartz plate (in saturated water vapour) and also on "wet" and then "dried" quartz plate. However, it is not quite clear why in the case of wetted in excess with water quartz plate, already after 4 min of the plate drying at 20 °C, the three-phase contact line should be treated to be at some distance from the bare surface of quartz. More experimental evidence must be obtained to find an answer for this question.

Symbols

γ_i	surface density of Gibbs energy of the i-th phase
γ_S	surface density of Gibbs energy of the solid
γ_L	surface density of Gibbs energy of the liquid
$\gamma_{S/L}$	interfacial density of Gibbs energy between solid and liquid phase
γ_Q	surface density of Gibbs energy of quartz
$\gamma_{Q/w}$	interfacial density of Gibbs energy between quartz and water
γ_w	surface density of Gibbs energy of water
$\Pi_{(I,II)}$	decrease in γ_Q behind the water droplet
$\gamma_{(Q,I)/w}$	interfacial density of Gibbs energy of quartz with water film I in contact with water
Θ	contact angle
Π_I	reduction of γ_Q under the water droplet
$\Pi_I(d)$	reduction of γ_Q caused by dispersion component
$\Pi_I(p)$	reduction of γ_Q caused by polar component
$\gamma_Q(d)$	dispersion component of γ_Q
$\gamma_Q(p)$	polar component of γ_Q
Π_{II}	part of $\Pi_{(I,II)}$ resulting from difference between $\Pi_{(I,II)}$ and Π_I

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