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Spreading of a water drop on a marble surface

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Measurements of the wetting contact angle for a marble surface were carried out for two systems: dry marble plate–water drop–saturated water vapour and marble wetted by water–water drop–dry air (in the presence of molecular sieves). The marble plate was placed in a measuring chamber and contact angles were measured after different lengths of time; it was found that their values grew to a maximum which was reached after about 30 min. It was found that when the dry marble plate was placed in saturated water vapour for 24 h the contact angle decreased in comparison with its maximal value. To explain the results obtained, theoretical calculations were made. The theoretical calculations and measurements showed that it was possible to obtain a contact angle greater than zero on a marble surface, depending on the structure and thickness of the water film.

1. Introduction

When a liquid drop is settled on a smooth, horizontal and dry solid surface, spreading may occur in two stages [1, 2]. In the first stage a thin film of liquid is formed and in the second the main process of spreading occurs. A thin film of liquid on a solid surface may be formed, either by adsorption of liquid vapour or by diffusion of liquid molecules from the drop periphery [2, 3]. The surface free energy of a solid is decreased by the thin film of the liquid [3–6] and the magnitude of this decrease depends upon the nature of the solid and liquid. Accordingly, if the interfacial free energy between the solid and the film of liquid is equal to the sum of the interfacial free energy of the solid–liquid and of the liquid surface tension, the contact angle is zero (as implied by Young's Equation [4]). If the interfacial free energy between the solid and the film of liquid equals the surface tension of the liquid and the interfacial free energy of between the solid and liquid equals zero, the contact angle is also zero [7]. Hence, the properties of a film of liquid influence the wetting process, particularly for high-energy solids [3–6, 8]. Thus, in spite of theoretical presumptions about complete wetting of a solid by a liquid in the solid–liquid drop–vapour of liquid system, the contact angle could be greater than zero [9].

The solid–water system plays the main role in the wetting processes because of its usefulness in many branches of chemistry and technology. Solids may be divided into two groups with respect to their interaction with water: hydrophilic solids and hydrophobic solids. Solids with a good wettability by water are termed hydrophilic solids (i.e. the contact angle is zero).

In scientific literature marble is considered to be a hydrophilic solid [8]. In this paper we would like to show that this opinion is not true. Adsorption measurements show that the water film formed on a marble surface has a thickness of about 15 statistical monolayers of water molecules. In a film of this thickness water molecules have properties other than those of the bulk phase [10]. Calculations, made on the basis of these measurements, have shown that a water film two statistical monolayers thick decreases the surface free energy of marble so that the surface free energy of the marble–water film is equal to the sum of marble–water interfacial free energy and the surface tension of water, corresponding to a zero contact angle [10]. Hence for a water film thicker than two statistical monolayers, it may be assumed theoretically that the contact angle for the system marble–water film–water drop–vapour (air) is greater than zero.

To verify this, measurements of the contact angle in the systems: a "dry" marble plate–water drop–saturated water vapour and a marble plate immersed in twice distilled water–water drop–dry air (in the presence of molecular sieves), were carried out after keeping the marble plate in the measurement chamber for different lengths of time. In these cases the contact angles were greater than zero.

2. Theory

The conditions of the spreading process of a liquid on a solid surface are expressed by Young's Equation [4]. For a solid–liquid drop–vapour system in which a three-phase contact line lies near the solid surface (as shown in Fig. 1) this equation may be presented as follows:

$$\gamma_{SV} - \gamma_{SL} = \gamma_L \cos\theta \qquad (1)$$

where $\gamma_{SV} = \gamma_S - \pi e$ is the surface free energy of a solid with adsorbed liquid vapours (γ_S is the surface free energy of a solid in vacuum, πe is the magnitude of a solid surface free energy reduction by adsorption of liquid vapour), γ_{SL} is the interfacial free energy of solid–liquid, γ_L is the surface tension of the liquid and θ is the wetting contact angle measured through the liquid phase.

If a solid is covered with a polymolecular water film of a thickness h (Fig. 1b), Young's Equation for a

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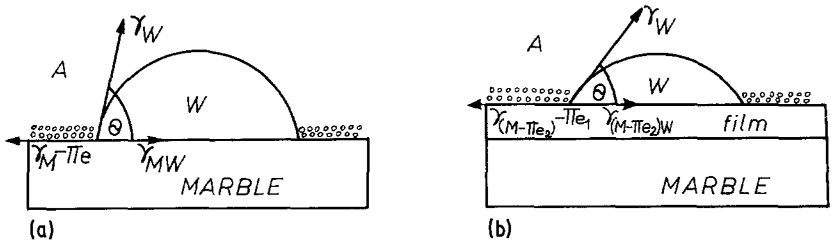

Figure 1 A scheme of the equilibrium state in the system marble–water drop–air. (a) Marble–water drop–saturated water vapour; (b) marble–water film–water drop–dry air. A = air, W = water drop.

water drop deposited on this film may be written in the following form:

$$\gamma_{SV(h)} - \pi e_1 - \gamma_{SL} - \pi e' = \gamma_L \cos\theta \qquad (2)$$

where $\gamma_{SV(h)} = \gamma_S - \pi e_2$ is the surface free energy of a solid covered with a polymolecular water film of thickness, h, πe_2 is the difference between the surface free energy of a solid and the surface free energy of a solid covered with a polymolecular water film, $\pi e'$ is the difference between the solid–water interfacial free energy and the solid–water film–water interfacial free energy and πe_1 is the magnitude of the reduction of the surface free energy of the water film on a solid by water vapour molecules adsorbed on this film. For $\gamma_{SV} = \gamma_{SL} + \gamma_L$ from Equation 1 it follows that a water drop completely spreads on a solid surface [4] (e.g. $\theta = 0$) (Antonow's rule). In this case we have:

$$\pi e = W_S = \gamma_S - \gamma_{SL} - \gamma_L \qquad (3)$$

where W_S is the work of spreading wetting. When $\pi e \leqslant \gamma_S - \gamma_L$ and $\gamma_{SL} = 0$, a water drop completely spreads. This is particularly valid for a system with $\gamma_S = \gamma_L$ and in which the surface free energy of the solid and liquid arises from the same kind of molecular interactions that are the same size in solid and liquid phases. Some authors [3, 4] suppose that for $\pi e = \pi e_2 = W_S$, $\gamma_{SV(h)}$ is always equal to the surface tension of liquid spreading on a given solid. However, measurements of water vapour adsorption on quartz suggest that W_S corresponds to a water film having a thickness of two statistical monolayers. On the other hand, Fowkes' theoretical calculations [11] and our earlier studies [12] prove that the value of the surface free energy of the quartz–water film of only 11 statistical water monolayers is equal to the water surface tension. This implies that for some solids $\pi e > W_S$ may be achieved and, therefore, the contact angle may be greater than zero for the system solid–water drop–water vapour. Let us consider Equations 1 and 2 once more for $\theta > 0$. If we assumed that γ_{SL} would be equal to $\gamma_{SV(h)} - \pi e_1$, then γ_{SL} would have to decrease to $\gamma_{SL} - \pi e'$ in the same time. Obviously Equation 2 does not exclude the possibility of complete spreading of a water drop on a solid surface. If for $\theta = 0$,

$$\gamma_{SV(h)} = \gamma_{SL} + \gamma_L - (\pi e_1 + \pi e') \qquad (4)$$

and if $\gamma_{SV(h)} \rightarrow \gamma_L$, then $\pi e_1 = 0$ and $\gamma_{SL} - \pi e'$ also equals zero. Thus from Equations 1 and 2 it follows (accepting our assumptions) that water can either completely wet a solid surface or form a contact angle greater than zero according to the properties of the water film on the solid. This conclusion suggests that under suitable conditions a water drop should not spread completely on a hydrophilic marble surface.

From the measured values of the wetting contact angle of a water drop on marble in *n*-alkanes and from the measurements of water vapour adsorption on marble its surface free energy was calculated [10]. Its value equals 170.6 mJ m^{-2} and is much higher than the surface tension of water (72.8 mN m^{-1}). Thus, according to many authors' opinions, maximal thickness of the water film formed by water vapour adsorption on a marble surface should cause water molecules occurring at the outermost points on the marble surface to have bulk phase properties, $\gamma_{MV(h)} = \gamma_W$ and $\gamma_{MV} = \gamma_{MW}$, where γ_{MV} is the surface free energy of marble covered with a polymolecular adsorption water film, $\gamma_{MV(h)}$ is the surface free energy of marble covered with polymolecular water film of thickness h, γ_{MW} is the free energy of the marble–water interface and γ_W is the surface tension of water.

Measurements of water adsorption have shown that the maximum thickness of the polymolecular water film is about 15 statistical monolayers, and the work of film formation is equal to the sum of the work of marble–water adhesion and the work of water cohesion [10]. On the other hand, the work of formation of the film having a thickness of two statistical monolayers corresponds to the spreading coefficient (work of spreading wetting W_S of water on marble surface) [10]. For this film and $\theta = 0$ according to Equation 1 we have $\gamma_{MV} = \gamma_{MW} + \gamma_W$. Since $\gamma_{MW} + \gamma_W > \gamma_M - \gamma_W$ the value of γ_{MV} for $\pi e = W_S$ is greater than γ_W. Thus a further decrease in γ_{MV} as a result of water vapour adsorption on the marble surface is possible. For $\pi e > W_S$ one may assume that a water drop does not spread on the marble surface and $\theta > 0$.

Expressing the interfacial free energy of marble–water by geometric mean of dispersion and polar interfacial interactions [6, 13] we obtain from Equation 1

$$\gamma_W \cos\theta = -\gamma_W + 2(\gamma_M^d \gamma_W^d)^{1/2} + 2(\gamma_M^p \gamma_W^p)^{1/2} - \pi e \qquad (5)$$

where γ_M^d and γ_W^d are the dispersion components of the surface free energy of marble and water surface tension, respectively, γ_M^p and γ_W^p are the polar components of the marble surface free energy and water surface tension, respectively. From Equation 5 values of θ may be calculated by changing πe from W_S to $\gamma_M - \gamma_W$, when [10]

$$\begin{aligned} W_S &= \gamma_M - \gamma_{MW} - \gamma_W \\ &= 2(\gamma_M^d \gamma_W^d) + 2(\gamma_M^p \gamma_W^p) - 2\gamma_W \qquad (6) \end{aligned}$$

When a water drop is deposited on the marble surface covered with a polymolecular water film of thickness h, Equation 5 may not serve for calculation of the equilibrium of the system marble–water drop–air. In such a case Equation 2 must be used for calculation of θ. In our previous paper [12] we suggested that

$$\gamma_{SL} - \pi e' = \gamma_{(S-\pi e_2)L} \qquad (7)$$

and [14]

$$\pi e_2 = \pi e_2^d + \pi e_2^p \qquad (8)$$

where πe_2^d and πe_2^p are the reduction of dispersion and polar components of marble surface free energy by the water film, respectively. Hence:

$$\gamma_{MW} - \pi e' = \gamma_M - \pi e_2 + \gamma_W - 2[(\gamma_M^d - \pi e_2^d)\gamma_W^d]^{1/2} - 2[(\gamma_M^p - \pi e_2^p)\gamma_W^p]^{1/2} \qquad (9)$$

Introducing Equation 9 into Equation 2 and assuming that $\gamma_{MV(h)} = \gamma_M - \pi e_2$ we obtain:

$$\gamma_W \cos\theta = -\gamma_W + 2[(\gamma_M^d - \pi e_2^d)\gamma_W^d]^{1/2} + 2[(\gamma_M^p - \pi e_2^p)\gamma_W^p]^{1/2} - \pi e_1 \qquad (10)$$

Next, according to our earlier assumption [14] we have:

$$\pi e_2 = 2(\gamma_M^d\gamma_W^d)^{1/2} + 2(\gamma_M^p\gamma_W^p)^{1/2} - x\gamma_W, \qquad (11)$$

$$\pi e_2^d = 2(\gamma_M^d\gamma_W^d)^{1/2} - x\gamma_W^d, \qquad (12)$$

$$\pi e_2^p = 2(\gamma_M^p\gamma_W^p)^{1/2} - x\gamma_W^p, \qquad (13)$$

and hence from Equation 10 with $\gamma_{MV(h(} - \pi e_1 = \gamma_W$ and $\gamma_{MV(h)} = \gamma_M - \pi e_2$, θ can be calculated with changing $\gamma_{MW} - \pi e'$ from γ_{MW} to 0.

Equations 5 and 10 appoint criteria for the non-spreading of a water drop on a marble surface covered with a polymolecular water film.

3. Experimental techniques

Measurements of the wetting contact angle on marble plates were conducted in a thermostated measuring chamber by means of a goniometer-telescope system at × 25 magnification. The marble plates of about 1 cm × 1 cm in size used for the studies were obtained from mineralogical specimens and were polished by rubbing one plate against the other. They were then washed several times in doubly distilled water, boiled for about 1 h in such water, dried at 250° C for 1 h and cooled to room temperature in a desiccator filled with molecular sieves (0.4 nm + 0.5 nm mixture).

For the first system thermostated at 20° C ± 0.1° C the measuring chamber was saturated with water vapour by placing in it a beaker containing doubly distilled water for 1 day. In the case of the second system, before measurement of the wetting contact angle, a mixture of molecular sieves 0.4 nm + 0.5 nm was placed in the measuring chamber for 1 day to decrease water vapour pressure to 10^{-5} mm Hg (10^{-5} mg dm^{-3}). When the plate had attained the environmental temperature (after drying) it was placed in the measuring chamber which was saturated with water vapour and the contact angle was measured immediately. After cleaning (which was repeated as above) the plate was placed in the measuring chamber and the contact angle was measured again after 6 min. Further measurements were made after the time periods shown in Table I. The last measurement was carried out when the plate had been in the measuring chamber filled with saturated water vapour for 24 h. Measurements for the second system were carried out as follows: cleaned and dried plates as presented above were dipped in doubly distilled water and placed in the measuring chamber in the presence of molecular sieves. The contact angle was measured after the time periods shown in Table I.

TABLE I Measured values of the wetting contact angle of a marble plate after different lengths of time in the measuring chamber for the systems dry marble plate–water drop–saturated water vapour and marble–water film–water drop–dry air, respectively

Dry marble plate		Wet marble plate	
Residence time in measuring chamber (saturated vapour) (min)	θ (deg)	Residence time in measuring chamber (dry air) (min)	θ (deg)
1	8	1	0
6	14	4	17.5
12	26.5	8	25
18	29.0	18	32
30	40.5	30	39.5
24 h	28.5		

4. Results and discussion

The results of measurements of contact angles for the two systems mentioned above are summarized in Table I, which shows that in the system marble–water drop–saturated water vapour as well as in the system wet marble–water drop–dry air (in the presence of molecular sieves) the contact angles reach their maximal values (40.5° and 39.5°, respectively), depending on the time periods after which the contact angles were measured. The maximum values of the wetting contact angle were obtained for $t = 30$ min. When the marble plate was placed in the measuring chamber for 24 h the value of θ measured for the system marble–water drop–saturated water vapour was lower than the maximum value for this system, which was only 28.5°. We assume that the wetting contact angle θ depends on the properties and the thickness of the water film on the marble surface. When a water drop is deposited on the marble surface covered with a polymolecular adsorption water film, it may spread depending on the value πe (see Equation 5). From this equation it follows that the wetting contact angle is zero when $\pi e = 76.6$ mJ m^{-2} (for $\gamma_M^d = 64$ mJ m^{-2}, $\gamma_M^p = 106.6$ mJ m^{-2}, $\gamma_W^d = 21.8$ mJ m^{-2} and $\gamma_W^p = 51.0$ mJ m^{-2}; these values were given by Jańczuk *et al.* [10]) and when πe increases from 76.6 to 97.8 mJ m^{-2} the contact angle increases from 0 to 44.9°. We assume that the maximum value of πe is $\gamma_M - \gamma_W = 170.6 - 72.8$ mJ m^{-2} $= 97.8$ mJ m^{-2}.

In Fig. 2a the wetting contact angle calculated from Equation 5 is presented as a function of πe. Comparing the values of θ from Fig. 2a and Table I, it may be found that the maximum value of θ calculated from Equation 5 (44.9°) is similar to the maximum measured value of θ for the two systems investigated (40.5° and 39.5°, respectively, see Table I). The variations of the calculated contact angle, being a function of πe are similar to the variations of the measured contact

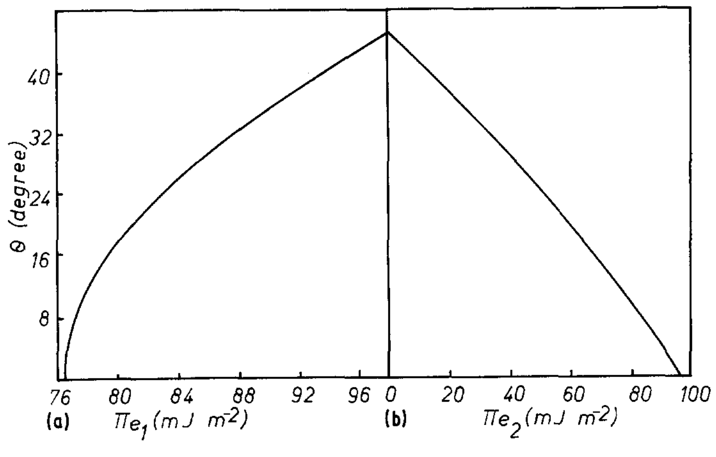

Figure 2 Relationship between a wetting contact angle and the water film pressure on the marble surface. (a) The relationship between a wetting contact angle and the water film pressure πe_1 for $\pi e_2 = 0$; (b) the relationship between a wetting contact angle and the water film pressure πe_2 for $\pi e_1 + \pi e_2 = \pi e_{\max} = \gamma_M - \gamma_W$.

angle, being a function of time for the system dry marble plate–water drop–saturated water vapour.

The agreement of these calculated contact angles with the measured values confirms our assumption that the surface free energy of marble covered with a polymolecular water film is relatively close to the surface tension of water. In contrast to the system mentioned above, it seems that to explain the obtained results of the contact angles for the second system it is necessary to assume that a rigid, highly oriented water film is present between the water drop and the marble surface. Hence, let us consider the contact angle variation in this system on the basis of Equation 10 for πe_2 values from 0 to 97.8 mJ m^{-2} when $\pi e_1 =$ 97.8 mJ m^{-2} $- \pi e_2$. Using values πe_2^{d} and πe_2^{p} calculated from Equations 11 to 13 and the above mentioned values of γ_M^d, γ_M^p, γ_W^d, γ_W^p and γ_W, it is possible to calculate the contact angle from Equation 10.

The contact angle as a function of πe_2 is presented in Fig. 2b. From this figure it appears that when the film thickness increases (and πe_2 values also increase) the contact angle decreases down to 0 for $\pi e_2 =$ 97.8 mJ m^{-2} (i.e. when the free energy of the marble–water film–water interface attains the value of γ_{MW}).

The changes of θ as a function of πe_2 are similar to the changes of θ for the system wet marble–water drop–dry air as a function of time (t) (see Table I). It is very characteristic that the value of the contact angle (28.5°) measured for a water drop deposited on the marble plate which was placed in saturated water vapour for 24 h, is equal to the value of θ calculated from Equation 4 for $\pi e_2 = 42$ mJ m^{-2}. However, the value of $\pi e_2 = 42.0$ mJ m^{-2} is similar to the pressure of the monolayer water film on the marble surface (46 mJ m^{-2}) [10], which suggests that after a long contact time of the marble surface with water vapour a highly oriented monolayer water film is formed. This was observed on quartz [5, 15]. The compatibility of the experimental and theoretical values of the contact angles implies that our assumptions are reasonable and suggests that the water film pressure on the marble surface and orientation effects of water molecules near the marble surface determine the wetting process of its surface.

References

1. W. B. HARDY, "Collected Works" (Cambridge University Press, Cambridge, 1936), p. 922.
2. D. H. BANGHAM and Z. SAWERIS, *Trans. Faraday Soc.* **34** (1938) 554.
3. W. D. HARKINS, "The Physical Chemistry of Surface Films" (Reinhold, New York, 1952) p. 41.
4. J. C. MELROSE, in "Wetting", Monograph No. 25. (Society of Chemical Industry, London, 1967) p. 123.
5. F. M. FOWKES (ed.), "Hydrophobic Surfaces" (Academic, New York and London, 1969) p. 191.
6. *Idem, Ind. Eng. Chem.* **56** (12) (1964) 40.
7. Y. KITAZAKI and T. HATA, *J. Adhesion* **4** (1972) 123.
8. A. D. ZIMON, "Adhesion of Liquid and Wettability" (Chim. Moscov, 1974) [in Russian].
9. W. A. ZISMAN, *Adv. Chem.* **43** (1964) 1.
10. B. JAŃCZUK, E. CHIBOWSKI and P. STASZCZUK, *J. Colloid Interface Sci.* **96** (1983) 1.
11. F. M. FOWKES, *ibid.* **28** (1968) 493.
12. P. STASZCZUK, B. JAŃCZUK and E. CHIBOWSKI, *Mater. Chem. Phys.* **12** (1985) 469.
13. S. WU, in "Polymer Blends", Vol. 1, edited by D. R. Paul and S. Newman (Academic, New York, 1978) p. 243.
14. B. JAŃCZUK, E. CHIBOWSKI and T. BIAŁOPIOTROWICZ, *J. Colloid Interface Sci.* **102** (1984) 533.
15. B. JANCZUK, *Przem. Chem.* **61** (1982) 468.

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