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Contact angle, hydrophobicity, hydrophilicity

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STUDY OF CONTACT ANGLE OF LIQUID ON SOLID SURFACE AND SOLID ON LIQUID SURFACE

The paper presents a study on the phenomenon of wetting of minerals in the two cases where a wetted solid is placed on a liquid surface and a liquid is on a flat solid surface. Knowledge of physical and chemical processes occurring between a liquid and solid is an important issue. Contact angle measurement and determination of interfacial tensions are very important in development of new technologies in which the gas-liquid-solid system appears. These problems are important for new solutions in many industries. The study confirms that many factors have an essential influence on the contact angle measurement.

1. INTRODUCTION

A contact angle is very important in flotation. Flotation is a process where a particle attaches to air bubble and the elevation of the resulting aggregate particle – bubble to the surface of the aqueous solution with higher density than the resulting aggregate. The binding capacity of the mineral particles to the air bubble depends on, among other, the wettability of the mineral surface. Only a particle hardly wettable with water, is attached to a gas bubble in contrast to a hydrophilic particle which is not attached and therefore, it does not float.

Hydrophobicity of a mineral surface, expressed in terms of contact angle depends on the strength of adhesion to the bubble (Drzymała, 2001). The contact angle is an important criterion for determining the degree of flotation of minerals particles. Many inorganic substances are hydrophilic. Sulfur, talc and teflon are considered to be highly hydrophobic substances (Jańczuk et al., 2005). Hydrophobic substances are usually organic compounds, especially crude oil and its derivatives. The easiest way to determine the hydrophobicity of a substance is to measure the contact angle. Hydrophilic materials have the contact angle equal to zero, because a liquid spreads on the

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surface, while for highly hydrophobic substances the angle reaches even 110 deg (Drzymała, 2001).

The flotation of hydrophilic or weak hydrophobic particles is improved by chemical reagents (collectors). Only for the flotation of naturally hydrophobic salt it is not necessary to use collectors and froth-making reagents (Ratajczak and Drzymała, 2003).

Some sulfite minerals and coal are regarded as medium or slightly hydrophobic, while calcite, hematite, quartz, magnetite are hydrophilic (Ratajczak and Drzymała, 2003, Szyszka, 2007). Figures 1 and 2 illustrate the behavior of liquid drop on solids, depending on the degree of hydrophobicity of material.

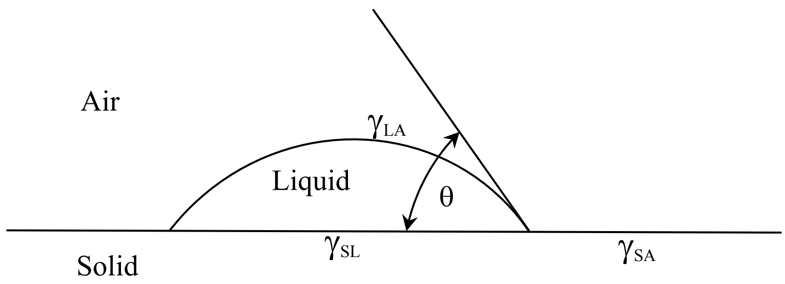

Fig. 1. The drop on a hydrophobic surface, with the graphical presentation of the Young equation

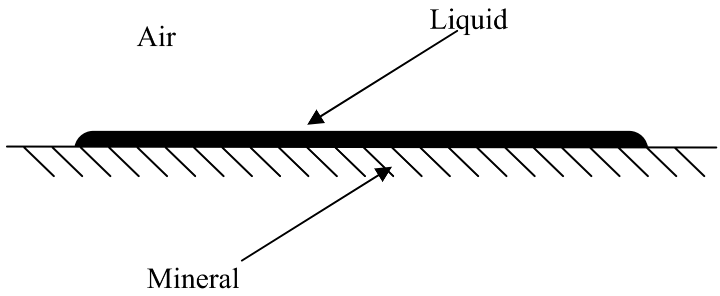

Fig. 2. The drop on the hydrophilic surface

The behavior of a liquid drop on solid surface depends on the forces acting within all three phases occurring within the system concerned, it is at the interface of water/solid, air/water and solid/air. These forces arise from interactions between atoms, ions or molecules in the adjoining phases. Issues related to surface tension had been widely discussed by Adamson (1990).

Molecules deeply set in liquids are balanced on all sides symmetrically by the forces of attraction exerted by the surrounding molecules. Particles present on the surface of the liquid are strongly attracted by liquid than gas. Consequently, the phenomenon of retraction of particles from the surface to inside of liquid is observed, which results in existence of a surface tension. The surface tension determines the liquid rising in the capillary and the formation of meniscus (Adamson, 1990). As a result, the surface tension of any liquid tends to have a minimal surface area to volume ratio that is a shape of a sphere (Drzymała, 2001). The equation describing the dependence of the angle formed by a drop placed on a solid surface described by Young's equation (Young, 1805), which is a

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta,$$

where: γ_{SA} – the interfacial energy at the phase boundaries of the solid (S)-air (A),
γ_{SL} – the interfacial energy at the phase boundaries of the solid (S)-liquid (L),
γ_{LA} – the interfacial energy (equal to the liquid surface tension) at the interfacial of liquid-air,
θ - the equilibrium contact angle, deg.

Water is common used liquid. The surface tension of water at 293 K is 72.8 mN/m. The addition of water to the surfactant reduces the surface tension results in wetting of highly hydrophobic solids (Jańczuk et al., 2005). Almost all of the special compounds used in the processes belong to surfactants. Their role in the processing of minerals is very important (Laskowski, 1969). Both the surface tension and contact angle depend on the type and concentration of a solution. With the increase in concentration of a solution of surfactant adsorption increases of the surface layer at the border of the solution - gas and simultaneously the drop in surface tension is evident. Under the influence of salt the increase of floatability is observed of the naturally hydrophobic mineral particles (Laskowski, 1969).

2. THE WETTABILITY OF SOLID SURFACES AND THE METHODS OF MEASURING OF THE CONTACT ANGLE

A wetting process strictly depends on properties of a surface of three contacted phases. It can be modified by the addition of surface-active liquid. To a large extent it also depends on the physical properties of wettable solid. The equilibrium state is achieved much quicker on unpours and uncrushed flat surface than on porous surface. The surface is characterized by high wetting and the degree of wetting is determined by the kinetics and thermodynamics of the wetting properties process (Jańczuk et al., 2005). The wetting can occur in three ways: spreading, immersion and adhesion. In the first case a liquid placed on a solid surface increases contact surface, displacing a gas phase from a solid surface.

In wetting adhesion, the liquid-solid contact surface does not change (Jańczuk et al. 2005). The basic methods for determining the contact angle consist of dynamometric and optical methods. The dynamometric methods are based on measuring torque forces engaging a solid plate through a liquid. The optical determination of the contact angle is based on observation of a liquid drop shape placed on a flat solid surface. The optical methods are based on the deformed shape due to interfacial tension forces, gravity and interfacial area. Many methods use image analyses obtained from the surveying camera and the measurement procedure for matching the contours of dimensionless theoretical solution of the Young-Laplace equation with actual contour (Adamson, 1990). The apparatus for such measurements are typically equipped with a digital imaging system, facilitating the measurement technique. It is also possible to determine a contact angle and a interfacial tension with an optical microscope and spherical particles of analyzed material in various sizes (Podgorski and Sosnowski, 2000). Issues related to the contact angle and its measurement had been widely discussed by Adamson (1990) and Drzymala (2001). The contact angle depends on both the measurement method, type of physical and chemical conditions of surface, as well as size of bubble and liquid droplets.

2.1. THE METOD OF THE SESSILE DROPS

The sessile drop method involves placing of liquid drop on a flat solid surface, and observing its shape.

The wetting of solid surface is determined by the method of the sessile liquid drop shown in Figure 3.

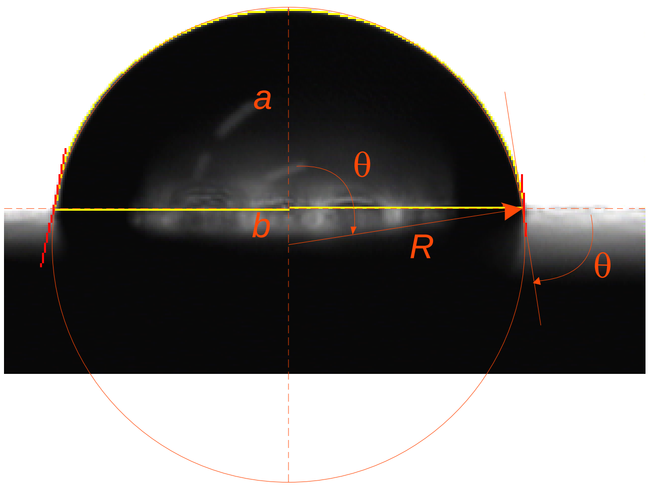

Fig. 3. The drop of water placed on the carbon surface

2.2. THE IMMERSION METHOD OF SPHERICAL PARTICLES

This method consists of determining the point where the tangent to spherical portion of a mineral is in a contact with the surrounding liquid. The angle is determined from the geometry, using the principle of similarity of triangles. The height of triangle from the top divides of the triangle into two triangles similar to each other and to the triangle. In immersion method, the line passing through the contact point of the phase boundaries, the theoretical radius of curvature of the spherical surface of the particles and the straight, perpendicular to the liquid surface form a triangle, which determine the contact angle. Graphical representation of this method presented in Figure 4.

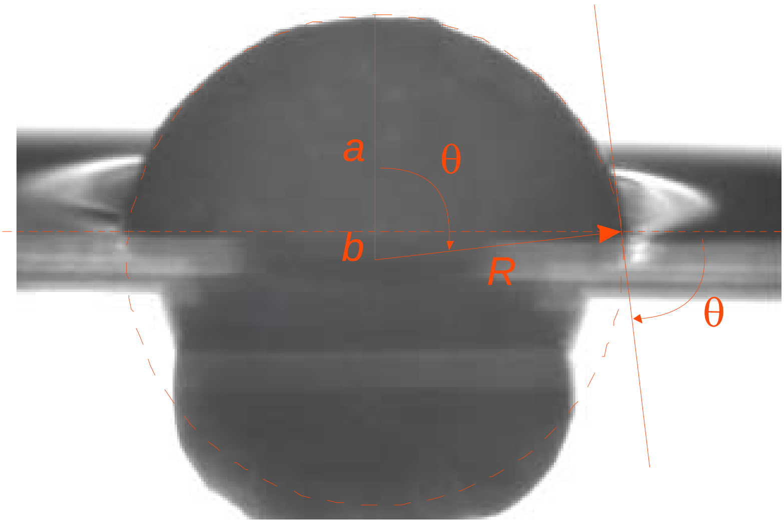

Fig. 4. Dependence of the size of contact angle on the immersion height of the spherical particle of sulfur in water. The liquid surface under the weight of the spherical particle

2.3. OTHER METHODS OF MEASUREMENT OF CONTACT ANGLE

There are also other methods of measuring the hydrophobicity of substances, such as inclined plate in the liquid (Heimenz, 1986), force of detachment (Heimenz,1986),, wetting the plate (Adamson,1976), levitation (Li at all, 1993), sessile drop on a pressed disk (Heertjes and Kossen, 1967; He and Laskowski, 1992), heat of wetting of particles (Neumann and Good, 1979), shape of the border of the aqueous phase (Aveyard and Clint, 1995)), thin layer wicking (van Oss at all, 1992), centrifuge (Huethorst and Leenaars, 1990)), the Washburn (Hołownia, 2008), and flotometric (Drzymala, 2001; Kowalczuk and Drzymala, 2011). The choice of method depends primarily on the measurement conditions. In this work we use sessile drop and solid on the liquid surface (surface flotation).

3. EXPERIMENTAL

3.1. METHODOLOGY

In this study the Phoenix 300 SEO system was used to measure the contact angle. It consists of Phoenix 300 instrument and Image XP software. Measurements were carried out at room temperature (20 ˚C).

The liquid drop was recorded using HDD camera. It gives information about theoretical contour of sessile drop and a immersed particle in a liquid. In this study, green color and white fluorite, gypsum, quartz, sulfur, and carbon were used. Distilled water was used as the wetting liquid.

The fragments of minerals were cut and polished with sand paper and cloth. Spherical slope of particles for immersed method were obtained by mechanical processing. The size is of maintaining the tested mineral on the surface of the liquid. The particles with size of 0.6–3.1 mm were used. The average diameter of the investigated particles are shown in Table 1.

Table.1. The average diameters of studied minerals

Mineral	The averaged diameter *d*, mm
sulphur	2.5
carbon	3.1
color fluorite	1.5
white fluorite	1.9
green fluorite	1.5
quartz	0.6
gypsum	1.9

3.2. MEASUREMENTS OF CONTACT ANGLE OF LIQUID ON SOLID SURFACE

The Image XP Software used in this study gives numerical values of the left and right contact angles. The average values of contact angle of tested materials were used in this work. In the case where the contact angle measurement was difficult, the slope of the tangent to the surface of placed drop was corrected manually. Moreover, calculations were done in this work with two different methods using trigonometric relationships cosine ($\cos\theta$), tangent ($\tan\theta$) and given by the tangent of the half ($\tan(\theta/2)$). Figure 5 shows graphical representation of measurement of contact angle for sessile drop..

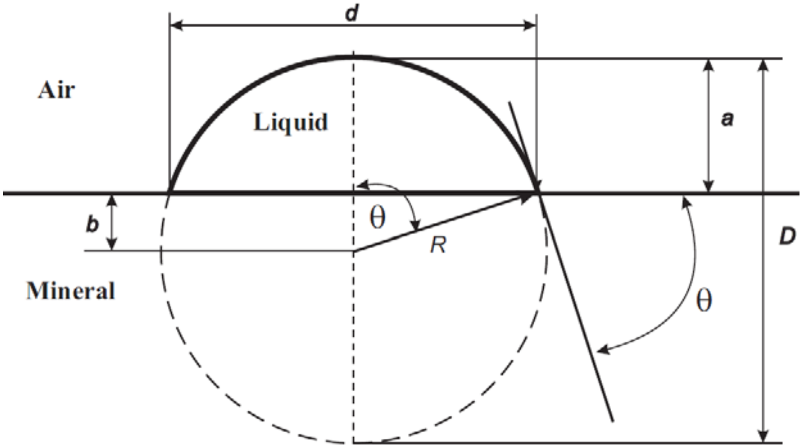

Fig. 5. The graphical representation contact angle measurements for sessile drop

The contact angle of material can be calculated from the following equations:

$$\cos\theta = \frac{b}{R} = \frac{R-a}{R}$$

$$\tan\theta = \frac{d}{2b} = \frac{d}{2(R-a)}$$

$$\tan\left(\frac{\theta}{2}\right) = \frac{2a}{d}$$

where: R – radius of spherical liquid drop, mm
a – height of the drop over the surface of the mineral, mm
b – distance from the center of the circle depicted on the drop to the surface of the mineral, mm
d – diameter of the base of the drop placed on the mineral, mm
θ – liquid contact angle, degrees
D – diameter of the circle described on the drop, mm.

Figures 6–12 show the liquid drop placed on solid (mineral) surface with the theoretical contour of drop surface and tangent to the point of joint fluid in three phases: liquid, solid and gas in the circle. It can be observed that the drops of water on different fluorite surfaces have different shapes. The contact angle of white and color fluorite was much greater than for green fluorite, what is shown in Figs. 6-8.

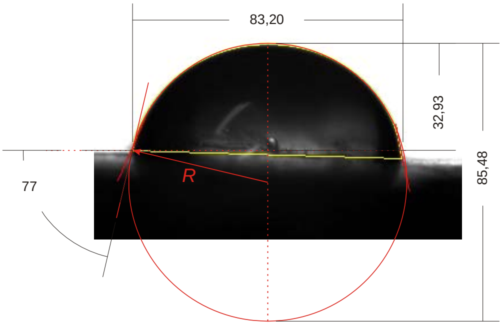

Fig. 6. Water drop on the surface of white fluorite

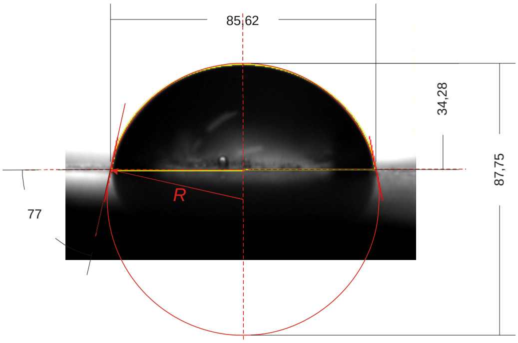

Fig. 7. Water drop on the surface of color fluorite

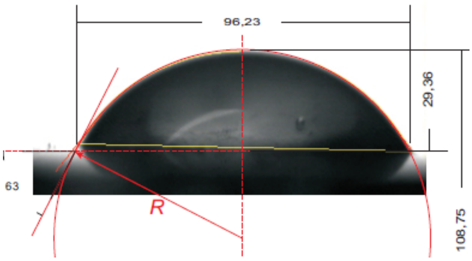

Fig. 8. Water drop on the surface of green fluorite

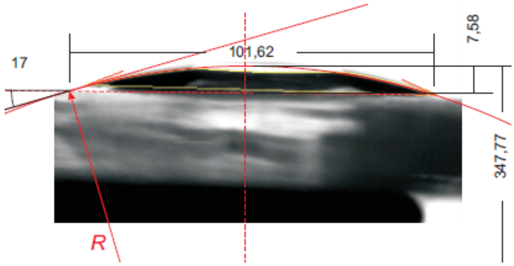

Fig. 9 Water drop on the surface of gypsum

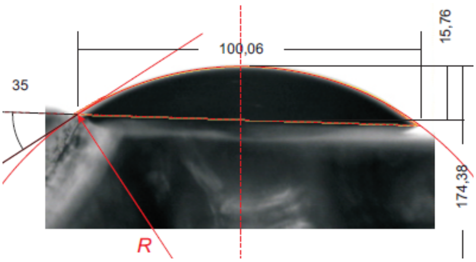

Fig. 10. Water drop on quartz surface

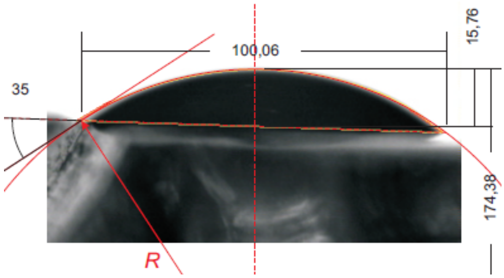

Fig. 11. Water drop on the surface of carbon

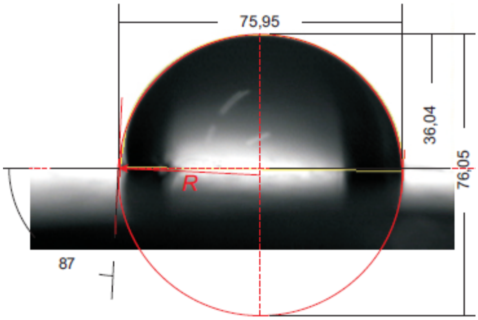

Fig. 12. Water drop on the surface of sulfur

Determination of contact angle on gypsum was very difficult due do its hydrophilic properties (liquid immediately spills all over the surface). Figure 11 shows that the contact angle gypsum is zero. It can be seen than quartz is more hydrophilic than different types of fluorite. From the shape of a drop of water placed on sulfur and carbon (Fig. 11 and 12) it can be said these materials are hydrophobic.

3.3. MEASUREMENTS OF CONTACT ANGLE OF SOLID ON LIQUID SURFACE

The contact angle was determined for spherical particle residing on the liquid surface. It is called surface flotation (Kowalczuk and Drzymała, 2012). Having the graphical solution sprayed onto the digital photo, it is possible to directly read the contact angle, or calculate it on the basis trigonometric function by working out cosine (cos θ) tangent (tan θ) and the tangent of the half (tan ($\theta/2$)) read from the distance of the part of the mineral protruding from the water.

Figure 13 shows graphical presentation of the dependence of the contact angle on the depth of immersion of spherical mineral particles.

The contact angle of the tested materials were calculated from the formulas given below

$$\cos\theta = \frac{b}{R} = \frac{R-a}{R}$$

$$\tan\theta = \frac{d}{2b} = \frac{d}{2(R-a)}$$

$$\tan\left(\frac{\theta}{2}\right) = \frac{2a}{d}$$

where: R – radius of spherical liquid drop, mm
a – height of the drop over the surface of the mineral, mm
b – distance from the center of the circle depicted on the drop to the surface of the mineral, mm
d – diameter of the base of the drop placed on the mineral, mm
θ – liquid contact angle, degrees
D – diameter of the circle described on the drop, mm.

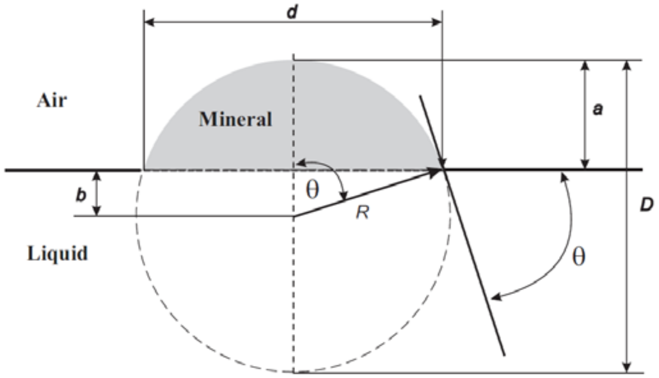

Fig. 13. Spherical solid on liquid surface when the weight of particle is neglected

Spherical hydrophobic particle with radius R placed on the liquid surface leads to deformation of the surface and meniscus occurs (Fig. 14 a). Then, we deal with non-equilibrium conditions and detachment (maximum liquid contact angle). When the weight of particle is neglected, we can assume a hypothetical situation that the line of contact of the liquid with the particle is not deformed (Fig. 14b), i.e. there is no concave meniscus, and then we measure the contact angle θ as an equilibrium contact angle θ_e (Kowalczuk and Drzymała, 2012).

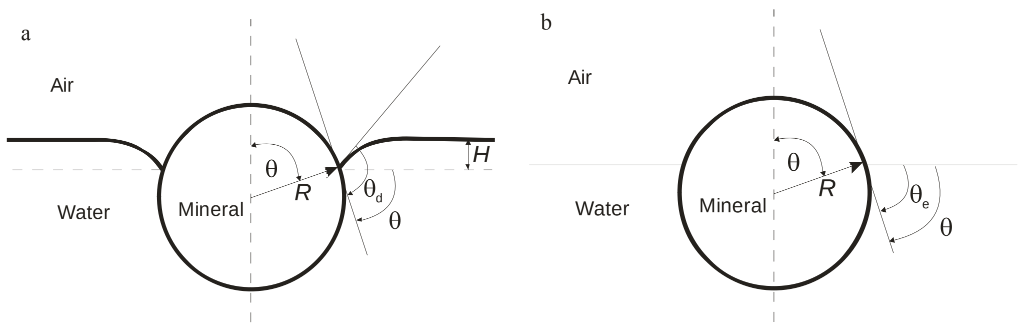

Fig. 14. Spherical hydrophobic mineral particle on the liquid –gas interface: (a) the deflection surface of the water – a concave meniscus (b) a theoretical situation where the line of contact of water with the mineral particle is not deformed (Kowalczuk, Drzymała, 2012)

The same relationship applies when the mineral is considered as hydrophobic or hydrophilic. The behavior of liquid substance in both cases is shown in Figure 14.

Figures 15-22 present contour of different spherical particles on liquid surface. The contact angle is included between the tangent to the spherical surface of mineral and the theoretical surface of liquid.

The data of the contact angle for white, color, green fluorite, gypsum, quartz, sulfur, and carbon were determined.

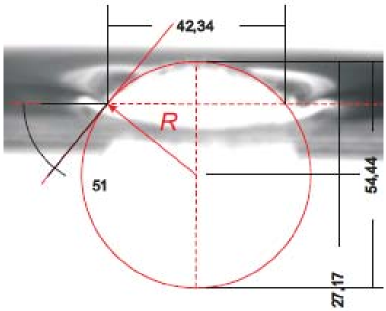

Fig. 15. Spherical particle
of white fluorite on water surface

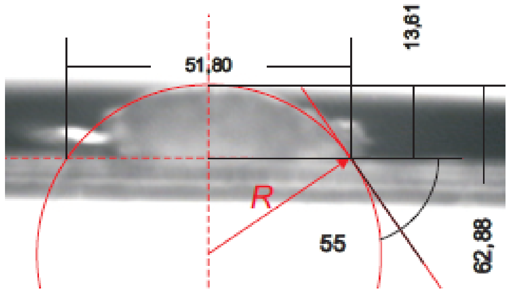

Fig. 16. Spherical particle
of color fluorite on water surface

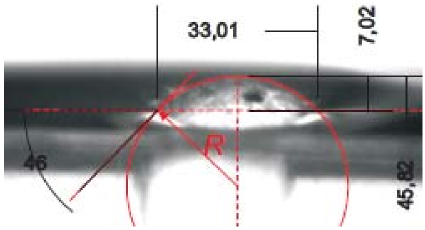

Fig. 17.Spherical particle
of green fluorite on water surface

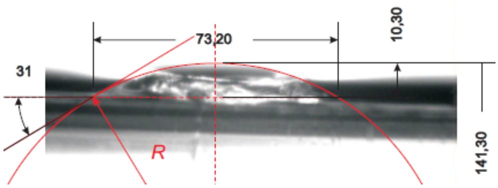

Fig. 18. Spherical quartz particle
on water surface

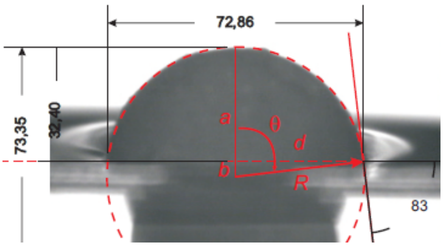

Fig. 19. Spherical particle
of sulfur on water surface

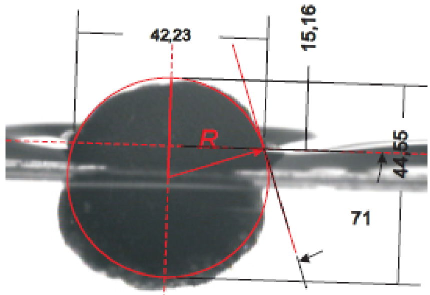

Fig. 20. Spherical particle
of carbon on water surface

Fig. 21. Spherical particle
of gypsum before contact

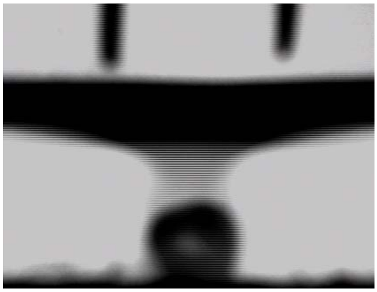

Fig. 22.Spherical particle
of gypsum under the water

4. RESULTS AND DISCUSSIONS

4.1. THE METHOD OF SESSILE DROP

The results of contact angle measurements and calculated data for sessile drop are presented in Table 2. The calculated data of contact angle for tangent and cosine are the same.

Table 2. Contact angle values measured and calculated for the sessile drop methods of measurement

Mineral	θ measured, °	θ_e calculated		
		$\cos\theta_e$, °	$\mathrm{tg}\theta_e$, °	$\mathrm{tg}(\theta_e/2)$,°
sulphur	87	87.0	87.0	87.0
carbon	81	81.1	81.1	81.1
color fluorite	77	77.4	77.3	77.4
white fluorite	77	76.7	76.7	76.7
green fluorite	63	62.6	62.5	64.8
quartz	35	35.0	35.0	35.0
gypsum	17	17.0	17.0	17.0

4.2. IMMERSION METHOD OF SPHERICAL PARTICLE ON LIQUID SURFACE

In the second series of measurements, the contact angle was specified and defined by the immersion method of spherical particles on liquid surface. The measurement of contact angle of gypsum, was not possible due to its hydrophilicity. Gypsum particles, regardless of their size, immediately sink.

Table 3. Contact angle values measured and calculated for the spherical particles immersion method

Mineral	θ measured, °	θ_e calculated		
		$\cos\theta_e$, °	$\mathrm{tg}\theta_e$, °	$\mathrm{tg}(\theta_e/2)$,°
carbon	71	71.4	71.4	71.4
color fluorite	55	57.5	55.4	55.4
white fluorite	51	51.1	51.1	51.1
green fluorite	46	46.1	46.1	46.1
quartz	31	31.6	31.4	31.5
gypsum	0	0	0	0

The results of the contact angle measurement (Table 3) are only marginally affected by the rough surface of spherical mineral that the mechanical treatment is natural. In this method as in sessile drop method the calculated data of contact angle for tangent and cosine are the same.

4.3. SUMMARY

The results indicate that among tested minerals the most hydrophobic is sulfur (Fig. 23). Carbon is also strong hydrophobic. From fluorites the most hydrophilic was green one. Quartz is characterized by very low hydrophobicity. Gypsum and quartz are minerals with the lowest contact angle.

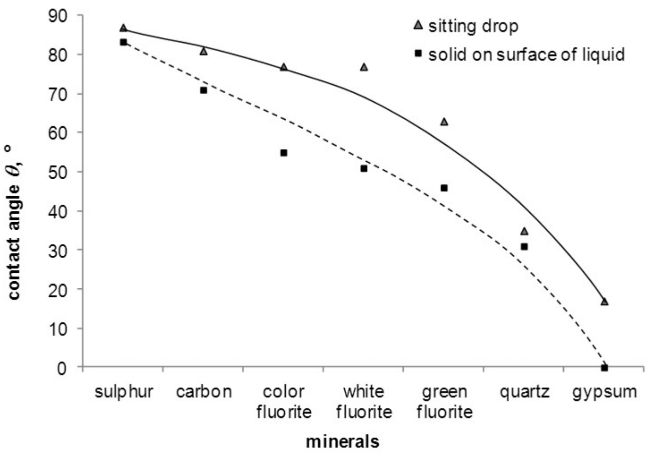

Fig. 23. Contact angle for different materials for sessile drop and solid on the liquid surface

The contact angle values taken from the both series of measurement retain correlation. It can be seen that different methods give different values of contact angles. It was also described by Drzymała (2001).

5. CONCLUSIONS

The above-described methods of determining the contact angle and the obtained results indicate that the sessile drop method gave a good reproducibility of the results for individual minerals.

The results of contact angles indicate that the sessile drop method gives a good reproducibility of results for minerals.

The applied method of measuring the contact angle of minerals consisting of immersion of the solid spherical particles on the surface of the contact liquid allows to achieve comparable results to the contact angle measurements of the contact angle values obtained by the sessile drop.

The methods used for calculating the contact angle of the trigonometric functions give exactly the same numerical value as the values measured by the applied program.

The method of immersion in the case of hydrophilic spherical particles materials such as gypsum, is difficult to implement because they sink.

The study confirms that many factors have a significant influence on the contact angle measurements. These factors include, among others: microroughness of surface, volume of drop and bubble, rate of drop deposition and accuracy in which the contour of sphere was determined.

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BADANIE KĄTA ZWILŻANIA CIECZY NA POWIERZCHNI CIAŁA STAŁEGO
I CIAŁA STAŁEGO NA POWIERZCHNI CIECZY

W pracy przedstawiono badania zjawiska zwilżania substancji mineralnych w dwóch przypadkach, gdy zwilżane ciało stałe znajduje się na powierzchni cieczy oraz gdy ciecz znajduje się na płaskiej powierzchni ciała stałego. Znajomość procesów fizykochemicznych zachodzących pomiędzy cieczą a ciałem stałym stanowi ważne zagadnienie technologiczne. Pomiar kątów zwilżania oraz wyznaczanie napięć międzyfazowych jest bardzo ważne w opracowywaniu nowych technologii, w których występuje układ gaz- ciecz- ciało stałe. Zagadnienia te mają istotne znaczenie dla nowych rozwiązań w wielu gałęziach przemysłu. Przeprowadzone badania potwierdzają, że wiele czynników ma istotny wpływ na wyniki pomiarów kąta zwilżania.