Short communication

SOME REMARKS ON ATTACHMENT OF A GAS BUBBLE TO ANOTHER PHASE BOTH IMMERSED IN WATER

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Abstract: In this paper the importance of definition of hydrophobicity and aquaoleophilicity in terms of contact angle as well as the properties of water films in flotation and oil agglomeration were briefly presented. It was shown that the hysteresis of contact angle for a considered system depends on the way of measurement and geometry of the system due to the presence of other that excess pressure and capillary forces and buffering properties of the capillary force. It was suggested that, the measured advancing and receding contact angles should be, when possible, recalculated into the Young (rest, equilibrium) contact angle. It was discussed that quartz is not a good model of hydrophilic surface because its contact angle with a gas phase in water is not zero and that a spontaneous attachment between highly hydrophobic materials such as hydrocarbons and Teflon in dynamic system, such as flotation, does not occur.

Introduction

Attachment of a gas bubble to either solid or liquid surface immersed in water is a crucial step in many processes such as flotation (Scheludko et al., 1976) and oil agglomeration performed in the presence of air (Drzymala et al., 1986). According to the second law of thermodynamics the process of attachment can take place only if the surface is not completely wetted by water, that is when the so-called contact angle is greater than zero. Then, the Gibbs potential of the three-phase contact is negative (Fuerstenau and Raghavan, 1976). On the other hand, according to the DLVO theory for flotation systems (Yoon and Mao, 1996) the kinetics of attachment depends on the properties of the bubble-surface interfacial region, that is on liquid films, and is determined by the energy barrier height of attachment. As a result, attachment can be spontaneous, slow or completely prevented. Thus, hydrophobicity and properties of

the liquid film are the most significant factors of the bubble-surface systems phenomena. These factors are frequently imprecisely defined and considered. In this article hydrophobicity and bubble-solid surface attachment issues will be briefly discussed.

Hydrophobicity

Hydrophobicity of a solid/gas/water system can be characterized by the so-called contact angle responsible for the appearance of a capillary force, the main force of bubble-to-surface adhesion. Depending on the field of science different hydrophobicity definitions, which are based on the contact angle, are used. In the colloid science the term hydrophobicity indicates that the three-phase contact angle of the solid/gas/liquid system, measured through the aqueous phase, is greater than 90 degrees (Bico et al., 2002; Bhushan, 2012). The system is referred to as hydrophilic when the contact angle is smaller than 90°. In mineral processing it is accepted that hydrophobicity starts when the contact angle of the solid/gas/liquid system, measured through the aqueous phase, is greater than zero (Nguyen and Schulze, 2004; Drzymala, 2007). It means that hydrophilic substances have the contact angle equal to zero. Thus, the definitions of hydrophobicity and hydrophilicity, when characterized by the contact angle, should be clearly indicated in scientific papers.

As it has already been mentioned, as a rule the contact angle is expressed through the aqueous phase (Adamson, 1990) and this approach is recommended for the three-phase systems involving solid-gas-water systems. It is also recommended to use in mineral processing the term hydrophobic for systems with the contact angle greater than zero. Otherwise, we will face the problem of strange expressions such as flotation of hydrophilic materials, because most naturally floating materials and minerals, which are rendered floatable by adsorption of surface modifying reagents (collectors) have the contact angle below 90° (Wark, 1938; Kowalczuk and Drzymala, 2011).

Sometimes it is very difficult, or even impossible, to tell if a substance is hydrophobic or hydrophilic because the measured contact angle is either zero or close to zero. This is so because the numerical value of contact angle for the same material depends on the way of measurements. It may result from the presence of slightly different forces involved in establishing the contact angle and geometry of the invested system. As a result the advancing, rest, receding and equilibrium contact angles are recorded. The difference between the advancing and receding contact angles measured for the same system and geometry is called hysteresis.

In calculations and considerations when only one value of contact angle is needed it is recommended to use the equilibrium (Young) contact angle, which for systems having well defined geometry can be calculated from the maximum advancing (detachment) contact angle (Drzymala, 1994a; Kowalczuk and Drzymala, 2012).

A good example of dilemma of hydrophobicity/hydrophilic is quartz. In some reports the contact angle of pure quartz is zero (Tarasevich, 2007; Wang et al., 2014), while numerous papers report that contact angle for quartz is greater than zero (Lamb and Furlong, 1982; Gee et al., 1990; Drzymala, 1994b). In our opinion quartz should be considered as weakly hydrophobic because it has a positive advancing, equilibrium, and in some studies also receding contact angles. In addition to that, quartz can float in the presence of selected frothers near its point of zero charge (Doren et al., 1975; Drzymala et al., 2007). Dahlgren et al. (1986) demonstrated that also there is a positive contact angle for captive air bubbles on glasses, which have very similar structure and properties to quartz. These observation suggests that the lack of quartz flotation in pure water (Drzymala, 1994c; Kowalczuk, 2015) does not results from quartz hydrophilicity but from the stable aqueous films present at the quartz/bubble interface. Thus, during important investigations it should not be ignored that quartz is a weakly hydrophobic material. In the case of a need to use truly hydrophilic materials other materials, including gypsum, should be used.

On one hand it is well known that contact angle depends on the method of measurement (Shang et al., 2008; Nowak et al., 2013). On the other hand it is claimed that there is no contact angle hysteresis on molecularly smooth surfaces. The case of mercury shows that this is not true because there is always a hysteresis of contact angle in real multiphase systems (Banerji, 1981; Xu et al., 1995). It results from very obvious facts that the Young equation, which defines the so-called equilibrium contact angle, is valid only for hypothetical systems, in which only excess pressure (Laplace equation) and capillary force are present. The angle of capillary force action is equal to the equilibrium contact angle determined by the energetics (and equivalent forces) of the three involved interfaces (Young equation). In real systems additional forces are always present which are counter-balanced by increasing capillary force due to the change of the contact angle from the equilibrium to either advancing or receding (Drzymala, 1994c). As a results of the additional, specific for given system forces and geometry, the contact angles are different even for the same systems but measured either by the sessile drop or captive bubble methods. Figures 1-3 illustrate this properties for different three-phase systems.

It should be noted that in the case of solid-water-oil systems it was recommended to use the terms aquaoleophilicity and aquaoleophobicity. In such systems the contact angle should be expressed through the oil phase (Yang and Drzymala, 1986). This recommendation is based on geometrical analogy between sessile water drop and sessile oil drop.
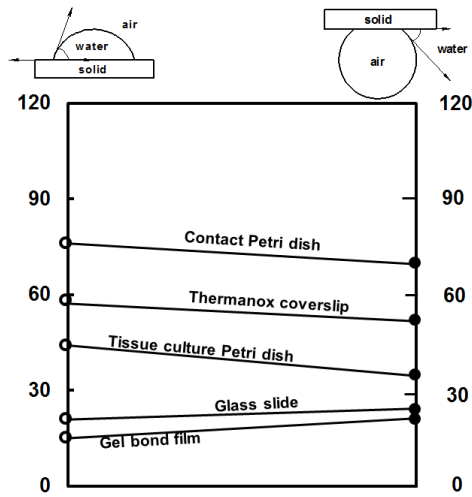
Fig. 1. Contact angle of glass-type materials measured in water drop-air-solid
and air bubble-water- solid arrangements. Dependence of contact angle value on the way
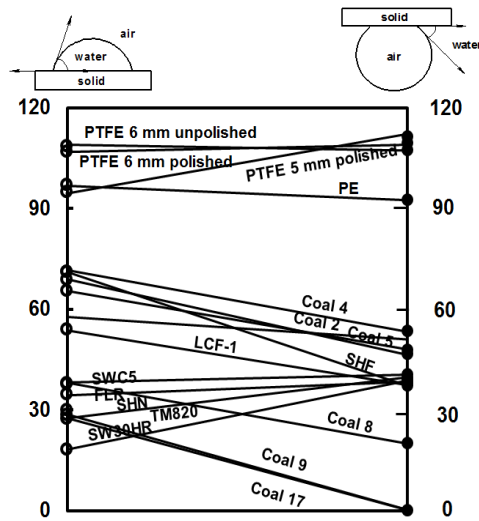of contact angle measurement is not visible. Source of data: Dahlgren et al. (1986)

Fig. 2. Contact angle of different materials measured in water drop-air-solid and air bubble-water- solid
arrangements. Dependence of contact angle value on the way of contact angle measurement is not visible.
Source of data: Drelich et al. (1996): PTFE 6 mm unpolished, PTFE 6 mm polished, PTFE 5 mm
polished, PE; Gutierrez-Rodriguez (1984): Coal 2, Coal 4, Coal 5, Coal 8, Coal 9, Coal 17; Baek et al.
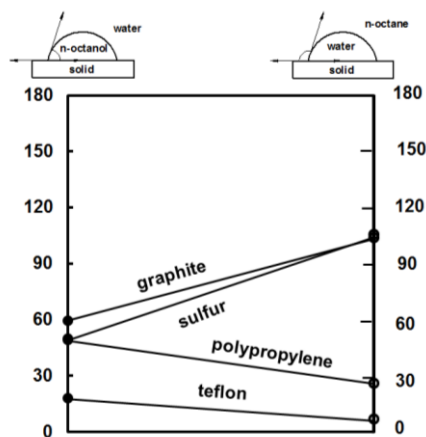(2012): LCF-1, SHE, SWC5, PER, SHN, TM820, SW39HR

Fig. 3. Contact angle of materials measured as water drop-n-octane -solid and as
n-octane drop-water- solid. Dependence of contact angle value on the way of contact angle
measurement does not occur. Source of data: Janczuk and Chibowski (1983): sulfur, graphite,
Teflon; Hamilton (1972), Chibowski and Holysz (1981): polypropylene

Bubble-solid surface attachment

Another important parameter of attachment of bubble to either highly hydrophobic solid surface or oleophilic material suspended in water is the kinetics of process. Wang et al. (2014) observed a spontaneous attachment of an air bubble to methylated quartz. It occurs only under static conditions since the kinetics of attachment under dynamic ones is totally different. Krasowska et al. (2006) and Kosior et al. (2011) showed that the bubble attachment to Teflon takes place only when, due to multiple unsuccessful collisions, the bubble reduces significantly its velocity. The same happens with other highly hydrophobic materials including high molecular mass hydrocarbons having contact angle up to 110°, as in the case of solid paraffin (Adamson, 1990). It was demonstrated by Medrzycka (1990) that nonvolatile highly hydrophobic hydrocarbons, including tetradecane, in the form of droplets suspended in water, do not float (Fig. 4). It means that the water film between oil drop and gas bubble is very strong.

Even though tetradecane is very hydrophobic, there is no a fast hydrocarbon-air bubble attachment during flotation. It means that the spontaneous attachment between the hydrocarbon and air bubble does not occur always and it is not present in many practical systems. Attachment occurs not spontaneously but with a certain rate due to repulsions caused by the aqueous films formed between the hydrophobic particle and air bubble. In the case of highly hydrophobic materials the attachment barrier is usually caused by electrical charges, which in the case of tetradecane droplets (Stachurski and Michalek, 1985; 1996) and bubbles (Li and Somasundaran, 1992) are both negative.
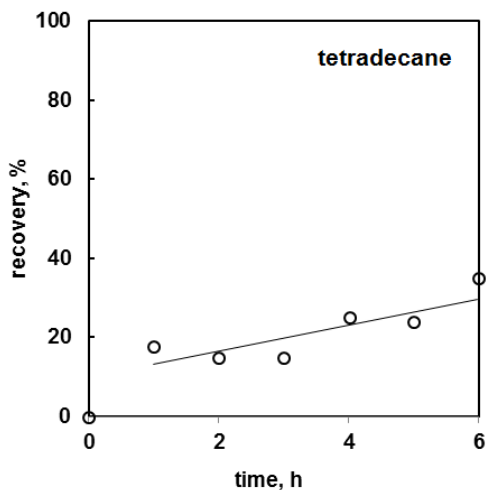
Fig. 4. Negligible flotation of suspended in water tetradecane droplets, even after
a long time of flotation. No spontaneous adhesion of highly hydrophobic
tetradecane to air bubbles occurs. The plot is based on the data of Medrzycka (1990)

Conclusions

Mineral processing papers dealing with hydrophobicity and aquaoleophilicity should specify the relation between these terms and contact angle. The hysteresis of contact angle for a system depends on the way of measurement and geometry (gas bubble, oil drop) of the system due to the presence of other that excess pressure and capillary forces and buffering properties of the capillary force. When possible, the measured advancing and receding contact angles should be recalculated into the Young (rest, equilibrium) contact angle.

Quartz in not a good model of hydrophilic surface because its contact angle with gas in water is not zero and that spontaneous attachment between highly hydrophobic materials such as hydrocarbons and Teflon in dynamic system such as flotation does not occur.

The presented remarks on the hydrophobicity of materials and kinetics of adhesion of highly hydrophobic materials to air bubbles should be helpful for considering these issues in research and review papers.

Acknowledgments

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