metals

Article

Wettability of Metals by Water

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Abstract: The wetting behavior of water on metal surfaces is important for a wide range of industries, for example, in the metallurgical industry during the preparation of metallic nanoparticles or electrochemical or electroless coating preparation from aqueous solutions, as well as in the construction industry (e.g., self-cleaning metal surfaces) and in the oil industry, in the case of water–oil separation or corrosion problems. Wettability in water/metal systems has been investigated in the literature; nevertheless, contradictions can be found in the results. Some papers have reported perfect wettability even in water/noble metal systems, while other researchers state that water cannot spread well on the surface of metals, and the contact angle is predicted at around 60°. The purpose of this paper is to resolve this contradiction and find correlations to predict the contact angle for a variety of metals. In our research, the wetting behavior of distilled water on the freshly polished surface of Ag, Au, Cu, Fe, Nb, Ni, Sn, Ti, and W substrates was investigated by the sessile drop method. The contact angle of the water on the metal was determined by KSV software. The contact angle of water is identified as being between 50° and 80°. We found that the contact angle of water on metals decreases linearly with increasing the atomic radius of the substrate. Using our new equation, the contact angle of water was identified on all of the metals in the periodic table. From the measured contact angle values, the adhesion energy of the distilled water/metal substrate interface was also determined and a correlation with the free electron density parameter of substrates was determined.

Keywords: wettability; adhesion energy; distilled water; metals

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1. Introduction

The wettability of metal surfaces by water is essential information for industry and chemical technologies, especially in the corrosion processes of metals, for electrode–electrolyte contact in the case of electrochemical syntheses [1,2], or in the oil industry in the separation of water–oil systems [3–10] and other applications, e.g., metallic nanoparticle preparation or corrosion behavior [11–15]. Several papers report on the study of the wettability in water/metal systems [16–21]. Nevertheless, contradictions can be found in the results, as Schrader [18] pointed out. White [22] believes that the contradictory results are due to the formation of an oxide layer of unknown composition and thickness on the surfaces during the cleaning processes, resulting in perfect wetting between water and metals. White [22] and Kaptay [23] point out that water cannot spread well on the surface of oxide-free metals, as the water and metal bond types are different, i.e., we expect good wetting in metallic liquid/metallic substrates or in ionic liquid/ionic substrate systems. In contrast, in water/metal systems, the contact angle (Θ) is generally assumed to be around 60°, which is supported by the results of the experiments by Erb carried out on noble metal surfaces [24]. The contact angle of water on gold at room temperature is about 62° [25]. However, quite different contact angles have been identified in other studies. The predicted water contact angle in [17] for Au is 0°, and the same angle is measured for Ag, Pd, and Pt. Low contact angles were measured by Trevoy and Johnson examining the wettability by the water of Al, Cu, Mg, Ni, stainless steel, and Zn; they found the contact angle was in the range of 5.0–9.1° for all the studied metals [16]. Against this, Mantel and Wightman measured the water contact angle on stainless steel, and the contact angle of water was found to be 49.5° [26]. They found a contact angle of ~10° on O_2-treated steel due to the formation of CrO_3. The water contact angle was reported on copper (Θ = 72° at 100 °C was measured) by Boyes and Ponter [27], who used Au, Pt, Ag, Cu, and Al as substrates, and the water contact angle was measured with different parameters [28]. Knowing the exact contact angle of the water/metal system is crucial in industrial prediction and modeling, for instance, in lubricant behavior investigation or in the flow of liquids [29–31] or in the surface wetting effect on cavitation formation [32], where better wetting leads to lower cavity formation. Additionally, the turbulent or laminar nature of the flow is influenced by the wetting behavior of the surfaces [33,34].

As this brief review reveals, studies have obtained very different results for the contact angle of water on metal surfaces. The literature does not provide a general equation to reliably predict the wetting behavior of metals by water or adhesion energy in water/metal systems.

The aim of our work is to determine the contact angle of distilled water on the surface of a wide range of metals and then to find a correlation between the contact angle and the characteristics of the substrate based on the measured data.

2. Materials and Methods

2.1. Sample Preparation

For the experiments, Ag, Au, Cu, Fe, Nb, Ni, Sn, Ti, and W were used. The 10 mm × 10 mm × 5 mm samples were prepared from the investigated metals (purity of the metals is 99.99%); these samples were the substrates. The metals were ground and polished mechanically; the average surface roughness (Ra) of the substrates was 0.02 μm (MARSURF M 400 Surface Roughness Measuring Instrument). In all cases, the surface of the substrates was polished immediately before the measurement.

2.2. Contact Angle Measurement

The experiments were carried out by the sessile drop method in equipment designed by Sunplant Ltd. (Miskolc, Hungary) (Figure 1).

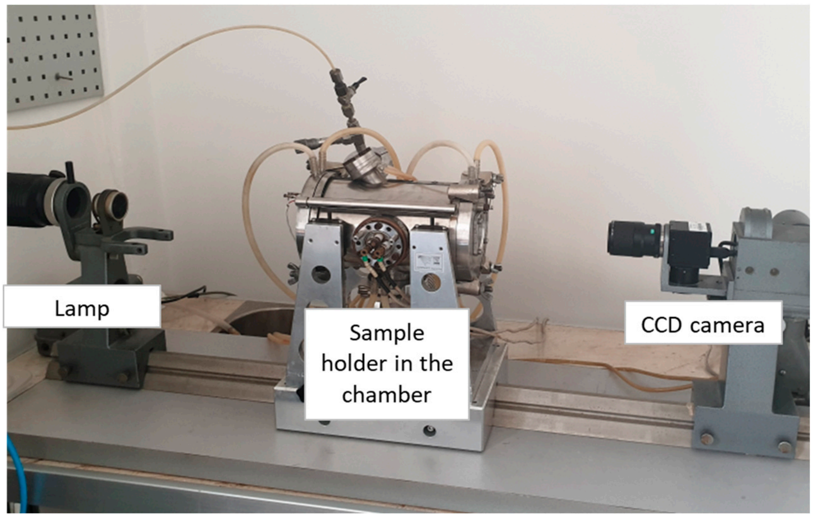

Figure 1. Equipment for the contact angle measurement.

In the contact angle measurement, a 5 μL distilled water droplet was placed on the surface of a polished substrate using an automatic pipette. The silhouettes of the formed droplet were photographed with a CCD camera, and the contact angle values were determined using KSV software (CAM2008, KSV Instruments Ltd., Helsinki, Finland). The contact angle values are shown as an average of 10 repeated measured data. The experiments were performed in an air atmosphere.

2.3. Validation of the Estimated Contact Angle

The estimation of the contact angles was validated in the cases of the Al, Si, Mo, and Hg. Al, Si, and Mo substrates, which were prepared according to Section 2.1, while Hg, for the substrate preparation, was poured into a Petri dish to minimize the curvature of the Hg surface. The contact angle measurement in all cases was performed according to Section 2.2.

Figure 2 shows a flowchart of the measurement process and analysis of the water contact angle on metal surfaces.

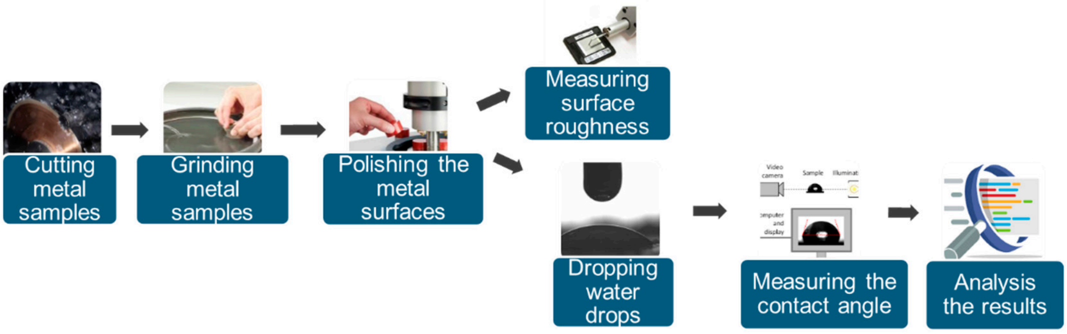

Figure 2. Flow chart of the measurement.

3. Results and Discussion

3.1. Relationship between Measured Contact Angles and Atomic Radii

The measured contact angle values of distilled water on the metal substrates are shown in Table 1.

Table 1. The measured contact angle on the surface of pure metals.

Substrate	Ag	Au	Cu	Fe	Nb	Ni	Sn	Ti	W
Contact angle, ±5°	64	62	72	72	57	73	65	62	63

In accordance with the results of White [22] and Kaptay [23], the contact angle of water on metal surfaces was found to be between 57° and 73° depending on the type of metal. Our results—that the contact angle on metal surfaces is not 0°—is also supported by the fact that microgrooves and micro-textures can improve the lubrication effect during water lubrication tests [30]. In the case of Θ = 0–5°, the liquid spreads perfectly on the surface, and there is no effect of microgrooving on the behavior of the liquid. If the contact angle is around 60°, the water spreads better due to the microgrooves.

The contact angle of the distilled water on metals as a function of the atomic number provides the periodic function shown in Figure 3. It can be seen that the contact angle follows the periodicity according to the periodic number of the substrate; opposite to this trend, the radius of the atoms of the substrate shows the periodicity.

From the opposite periodicity of contact angle and the atom radius of the substrate observed in Figure 3, it can be concluded that the atomic radius of the substrate affects the contact angle value measured on the surface of the substrate. Figure 4 shows the contact angle values as a function of the atomic radius of the substrate. The linear trend of the contact angle as a function of the atomic radius of the substrate is clearly shown.

Considering Figure 4, the contact angle of distilled water on different substrates, taking into account the atomic radius of the substrate, can be described for metallic substrates with the following relation:

$$\Theta = -0.582 r_A + 148, \quad (1)$$

where Θ is the contact angle of the distilled water (°) and r_A is the atomic radius of the substrate (pm) [35,36].

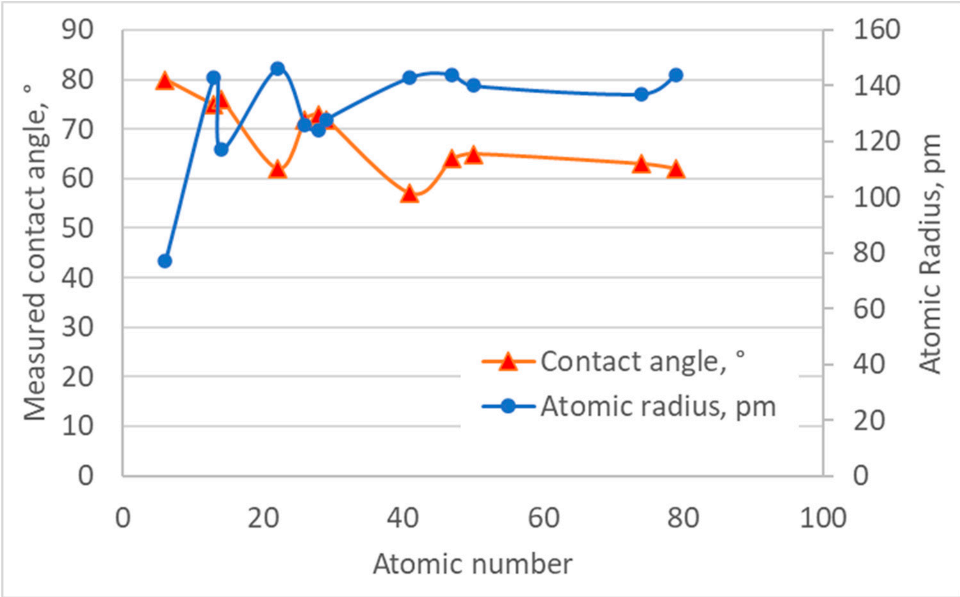

Figure 3. The measured contact angle of distilled water and radius of the substrate atoms as a function of the substrate atomic number.

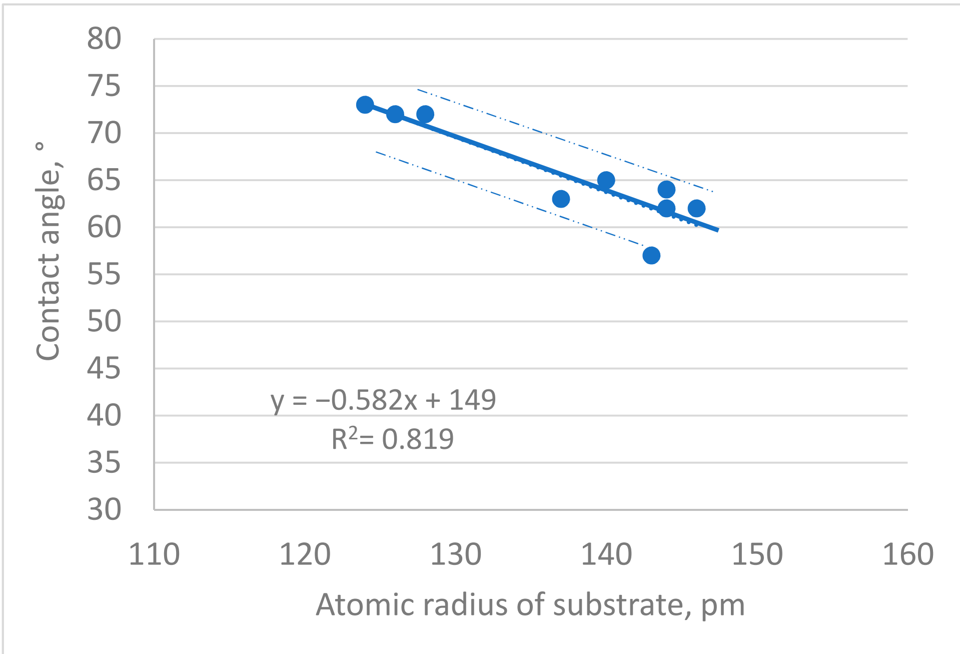

Figure 4. The contact angle of distilled water as a function of the atomic radius of the substrate.

Since water was used as the liquid phase, the question arises whether a chemical reaction may have occurred between the water and the substrate at room temperature, and the formed reaction product, an oxide, may possibly have affected the contact angle of water. In Figure 5, the free enthalpy of the formation of the possible oxides of the substrates is shown as a function of the atomic radius of the substrate. It can be seen that there is no mathematically descriptive relationship between the free enthalpy of formation and atomic radius (correlation coefficient r = −0.3991 and R^2 = 0.1593). This means that the observed wetting behavior is not affected by oxide formation. This is also supported by the fact that carbon fits well in the contact angle–atomic radius diagram (Figure 4) ($\Theta_{\text{waterCarbon}}$ = 80 ± 5°), while there is no chemical reaction between C and H_2O at room temperature.

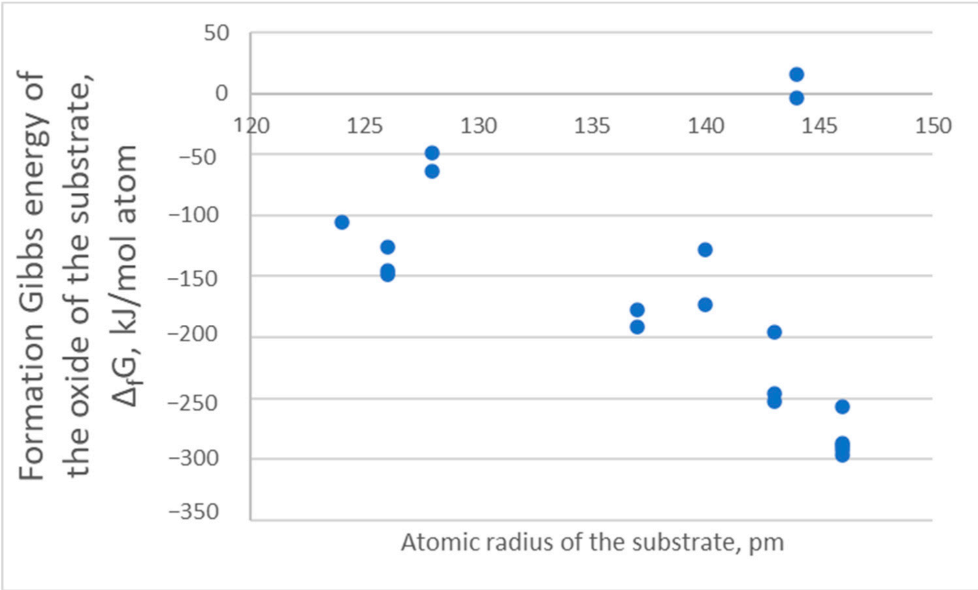

Figure 5. Free enthalpy of the formation of oxides [37] as a function of the atomic radius of the substrate.

3.2. Estimation of the Contact Angle of the Distilled Water for the Metals of the Periodic Table

Using Equation (1), it is possible to estimate the contact angle of the distilled water on the surface of the metallic and semi-metallic elements of the periodic table. The estimated contact angles on the metallic and semi-metallic elements are depicted in Figure 6. The estimated contact angles were validated with the contact angle measurement of distilled water on liquid Hg and polished surfaces of Al, Si, and Mo. The results of the measured and validated contact angle can be seen in Table 2. A good correlation can be seen between the measured and estimated data; they overlap within the uncertainty of measurement with an r = 0.8311 correlation coefficient.

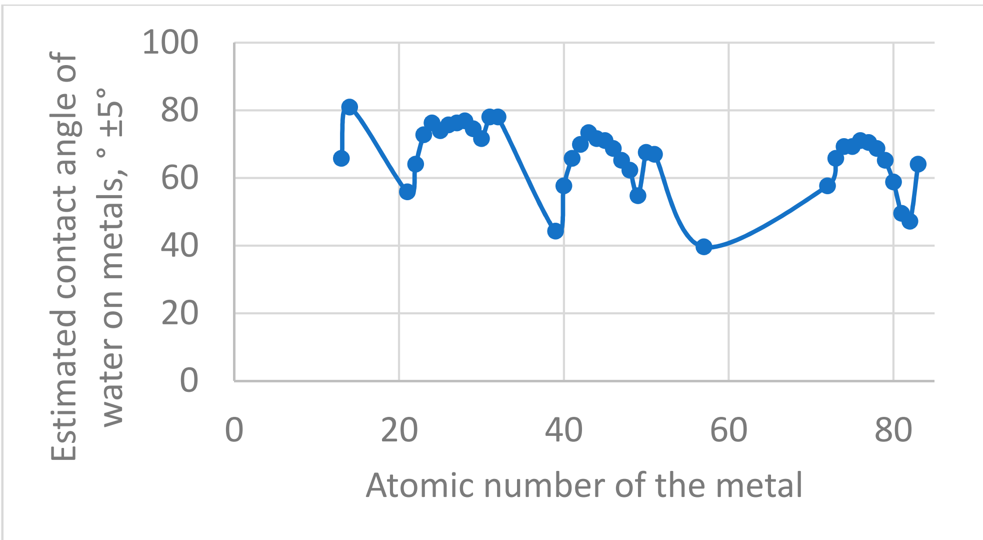

Figure 6. Contact angle values determined by Equation (1) as a function of the atomic number.

Table 2. Comparison of the estimated and measured contact angle of water on Al, Si and Mo surfaces.

Element	Estimated Contact Angle (Figure 6)	Measured Contact Angle
Al	$66 \pm 5°$	$71 \pm 5°$
Si	$81 \pm 5°$	$76 \pm 5°$
Hg	$59 \pm 5°$	$58 \pm 5°$
Mo	$70 \pm 5°$	$76 \pm 5°$

3.3. Water/Metal Adhesion Energy

The adhesion energy of the water/metal system can be identified using the contact angle of the water by using the Young–Dupré Equation (2):

$$W = \sigma_{lv} \cdot (1+\cos\Theta) \tag{2}$$

where W is the adhesion energy (J/m^2), $\sigma_{lv}\cdot$ is the surface tension of the liquid phase (J/m^2), and Θ is the contact angle (°). The wettability of metals and thus the adhesion energy of the water/metal system must also depend on the charged particles located on the surface of the substrate. The metallic substrates have different free electron densities [38], which affect the wetting behavior. The calculated adhesion energy values of the water/metal system (based on Equation (2)) are depicted as a function of the free electron density parameter (Figure 7) according to the W~ f(r_S^{-4}) correlation. The r_S^{-4} was established in the work of Wojciechowski [39]; the values of the free electron density (r_S) are from Perrott and Rasolt [40]. In Figure 7, a good correlation can be seen between the adhesion energy of the water/metal system and the free electron density parameter (r_S^{-4}) of the metals. We can say that the free electron density of the metal substrate determines the adhesion energy of the water/metal system. The correlation is

$$W = \pi . r_S^{0.62} \tag{3}$$

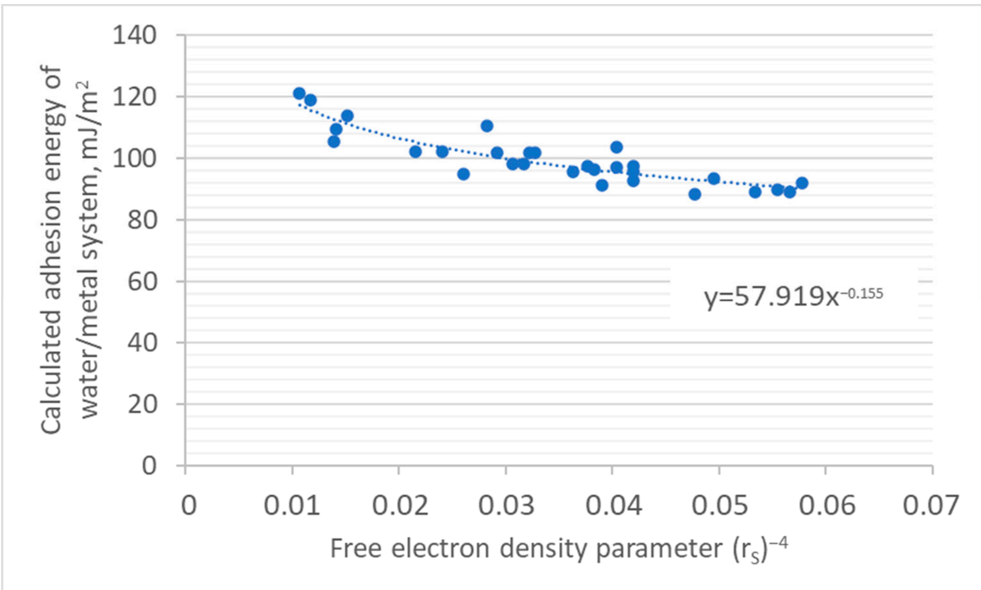

Figure 7. Adhesion energy (W) as a function of the free electron density parameter following the W~f(r_S^{-4}) correlation.

The calculated adhesion energy values are checked against Equation (3) in Figure 7. A good correlation can be seen with the semi-empirical coefficient of Equation (3): $\pi \approx 58$ mJ/m^2. The correlation coefficient between the free electron density parameter and the calculated adhesion energy is -0.8648, which means that there is a strong correlation between the data.

4. Conclusions

The aim of this investigation was to determine the wetting behavior of the metals and the adhesion energy values in water/metal systems. Furthermore, our goal was to establish new semi-empirical models for the prediction of the contact angle and adhesion energy in water/metal pairs. Our results are summarized in the following points.

- Using Ag, Au, Cu, Fe, Nb, Ni, Sn, Ti, and W as substrates, the contact angle of the distilled water on the polished surface of the substrates was determined.
- A new linear relationship was identified between the atomic radius of the substrate element and the contact angle of distilled water.
- An equation was created (Equation (1)) to estimate the contact angle of distilled water on the surface of the metals and semi-metals of the periodic table. The estimated values were validated with contact angle measurement on Al, Si, Hg, and Mo.
- The calculated adhesion energy of water/metal systems correlated well with r_S^{-4} (the free electron density parameter) according to Equation (3).
- These new observations can be used in the preparation of metallic nanoparticles and in water–oil separation.

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