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Article

Wettability of Polar and Apolar Liquids on Metal Surfaces

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Abstract: The wettability of metal surfaces by different oils and water is a multifaceted phenomenon with significant implications for industrial processes, including lubrication, corrosion protection, and fluid transport; an understanding of the process is essential for optimizing the performance and durability of metallic components. The intermolecular interactions between oil molecules and the metal surface primarily influence the wetting of a metal surface by different types of oil. This paper introduces the concept of oil wetting on metal surfaces, exploring the factors influencing wetting behavior, the characterization techniques employed to assess wetting properties, and the implications for different industrial processes. This work aims to ascertain the contact angle of oil on various metal surfaces and subsequently establish a relationship between this contact angle and the attributes of the substrate. This is achieved through using the sessile drop technique. The results indicate that the wettability of petroleum was better than the hydraulic oil we used on all types of substrates (for example, on Ag surface, Θ-petroleum = 11°, but Θ-hydraulic oil = 20°). Also, we observed that the cosine of the oil/metal contact angle increases with the increase in the atomic radius of the pure metal substrate, and Becker's broken bond model proved this linear relation. We then contrast this behavior with the wetting characteristics of water and glycerin on the same metals using the same conditions.

Keywords: wettability; oil/water separation; metals; adhesion energy

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1. Introduction

When metal surfaces come into contact with oil, intermolecular forces interact, dictating how the oil spreads on the surface. This phenomenon, wetting, holds paramount importance in materials science and engineering. It entails how a liquid adheres to and spreads across a solid surface [1,2]. The ability of oils to wet metal surfaces significantly influences the performance and durability of metallic components across diverse industries. Hence, obtaining a comprehensive grasp of the factors that affect oil wetting on metal surfaces is imperative for refining industrial procedures [3–5]. Numerous investigations have indicated that the surface energy of the oil and the metal surface determines the extent of oil wetting [6–8]. The equilibrium between adhesive and cohesive forces significantly affects the contact angle and spreading behavior of the oil on the metal surface.

Beyond this, Quéré [9] and Wang et al. [10] have investigated another variable, the roughness of the metal surface. This factor influences the effective contact area between the oil and metal, influencing wetting behavior. Surface roughness modifies the observable contact angle and can lead to either heightened or diminished oil wetting. Meanwhile, Zhu et al. [11] delved into surface chemistry, demonstrating that the chemical composition and functional groups present on the metal surface can influence oil-wetting behavior. Alterations in surface chemistry through treatments and modifications can subsequently impact the contact angle and spreading behavior of the oil [12,13]. In industrial contexts, knowing the precise contact angle of the oil/metal system holds pivotal importance. It aids in predictive modeling for industrial applications such as investigating lubricant behavior, fluid flow dynamics [14–17], and oil–water separation [18,19], where divergent wetting behaviors can lead to effective oil–water separation. This knowledge proves indispensable in industries and chemical technologies, especially in metal corrosion processes, the oil sector's water–oil separation [20–23], and other applications, like preparing metallic nanoparticles or studying corrosion behavior [24–26]; moreover, the manufacturing and quality assurance process for wafers of solar cells also includes contact angle measurement [27].

The wettability of oil and water on metal surfaces is important in the case of oil pipelines; surface wetting can impact cavitation formation, with enhanced wetting diminishing cavity formation. The flow's turbulent or laminar nature is influenced by surface wetting behavior [28,29]. Previous studies reveal a spectrum of outcomes regarding the contact angle of various oil types on metal surfaces compared to the behavior of water wetting. In several research papers [30–35], contradictions arise regarding wettability behavior within oil–water systems. These inconsistencies can be attributed to creating an oxide layer with uncertain composition and thickness during cleaning procedures. This layer contributes to establishing ideal wetting between metals and water, a phenomenon supported by White's research [36]. These studies focused only on the effect of water wetting on metals and did not address the impact of oil wetting, a major water partner in the oil industry.

There is no study that has investigated the effect of the atomic radius of metals on the wettability behavior of polar and apolar liquids, with the exception of [37], which only focused on the effect of the atomic radius on the wettability behavior of water. Here we study the effect of the atomic radius of the metals on the wettability behavior of another polar liquid (glycerin) in addition to water and on two apolar liquids (hydraulic oil and petroleum) and compare the results with the results of [37].

This study presents experimentally derived contact angle distributions for different oil types on metal surfaces. Its aims are to better understand how contact angles evolve during repeated spreading on metal surfaces and to ascertain the contact angle formed by water, glycerin, hydraulic oil, and petroleum on various metal surfaces. Based on this, we attempt to establish a relationship between this contact angle and the underlying substrate's attributes.

2. Materials and Methods

2.1. Preparation of the Samples

For the wetting test, we used pure metals as substrates. Ni, Cu, Ag, Al, W, Sn, Fe, and Cd were used as substrates with 99.99% purity, and the size was 10 mm × 8 mm × 5 mm in all cases. The substrates were ground and polished mechanically immediately before the measurement. The average surface roughness of the substrates (Ra) was 0.02 µm using a surface roughness measurement device (MARSURF M 40). The preparation was made at room temperature and normal air, and relative humidity was ~56%.

2.2. The Measurement of the Contact Angle (CA)

In our research, we used the sessile drop method to determine the contact angle of distilled water, glycerin, hydraulic oil (HME10 from MOL Group), and refined petroleum (MOL Group) (88–92 w% hydrocarbon, C10-C13, n-alkanes, iso-alkanes, cyclic compounds, <2% aromatics, 8–12 w% hydrocarbon, C15-C20, n-alkanes, iso-alkanes, cycloalkanes,

<0.03% aromatics) separately. Using an automatic pipette, a drop of 5 μL of liquid was placed on the surface of a polished substrate for 5 min for each sample. A CCD camera was used to record the changes in the silhouettes of the formed drop. The CCD camera was connected to a computer with KSV software (CAM2008, KSV Instruments Ltd., Helsinki, Finland) to determine the value of the contact angle. The experiments were performed at room temperature, and the liquid contact angle values (measured data) were repeated at least ten times for each sample.

The process of measuring and analyzing the liquid contact angle on metal surfaces is depicted in Figure 1. The experimental procedures were conducted using the sessile drop technique, utilizing equipment developed by Sunplant Ltd. (Miskolc, Hungary).

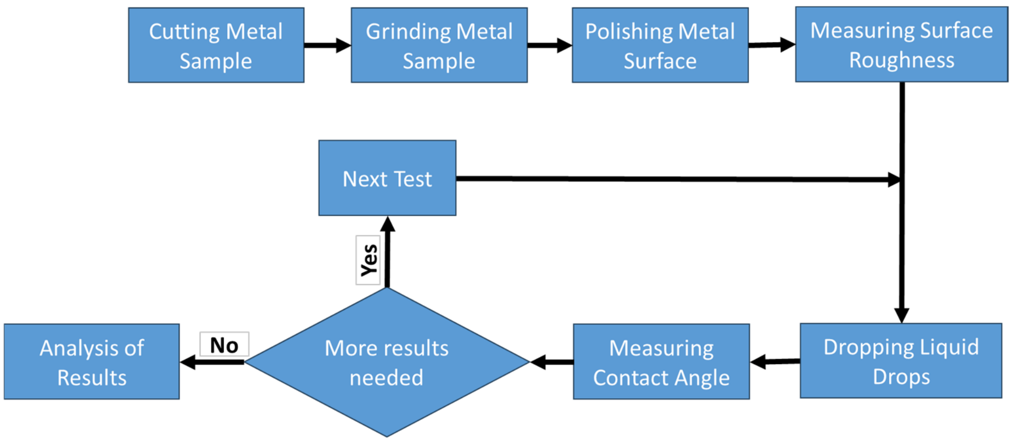

Figure 1. Measurement process.

3. Results and Discussion

3.1. Experimental Results

We focused on polar and apolar liquids in this research; the results of the wettability test are collected in Table 1. Firstly, we remeasured the contact angle of distilled water, which is between 63° and 77°; results show that water does not readily spread on the surface of metals that are free from oxide layers, confirming results in [37]. Averaged values are shown here; deviation is ±3°.

Table 1. The measured contact angle θ (in degrees) of the liquids on the surface of pure metals.

Liquid	Al	Fe	Ni	Cu	Sn	Ag	W	Cd
Hydraulic oil	20	12	8	15	19	20	18	22
Petroleum	9	3	2	5	9	11	8	11
Distilled water	69	77	80	78	70	67	71	63
Glycerin	73	80	84	82	75	72	76	69

Glycerin, which differs in viscosity and density from water, has a contact angle of about (69–84°). Figure 2 shows the silhouettes of the contact angle and its measurement. Figure 2a has a similarity in the wettability function of the water on the same metal surfaces; the reason is that both water (72 mN/m) and glycerin (64.7 mN/m) have relatively high surface tensions, and liquids with higher surface tension tend to form rounded droplets on surfaces to minimize their surface area. Water is inherently a highly polar molecule, resulting in a partial positive charge on its hydrogen atoms and a partial negative charge on its oxygen atom. This polar nature enables water molecules to create hydrogen bonds not only with each other but also with other polar molecules, such as those found on various solid surfaces. Glycerin also has polar hydroxyl (-OH) groups, which can form hydrogen bonds with water molecules and with solid surfaces; these hydrogen bonding interactions contribute to the wetting behavior of both substances.

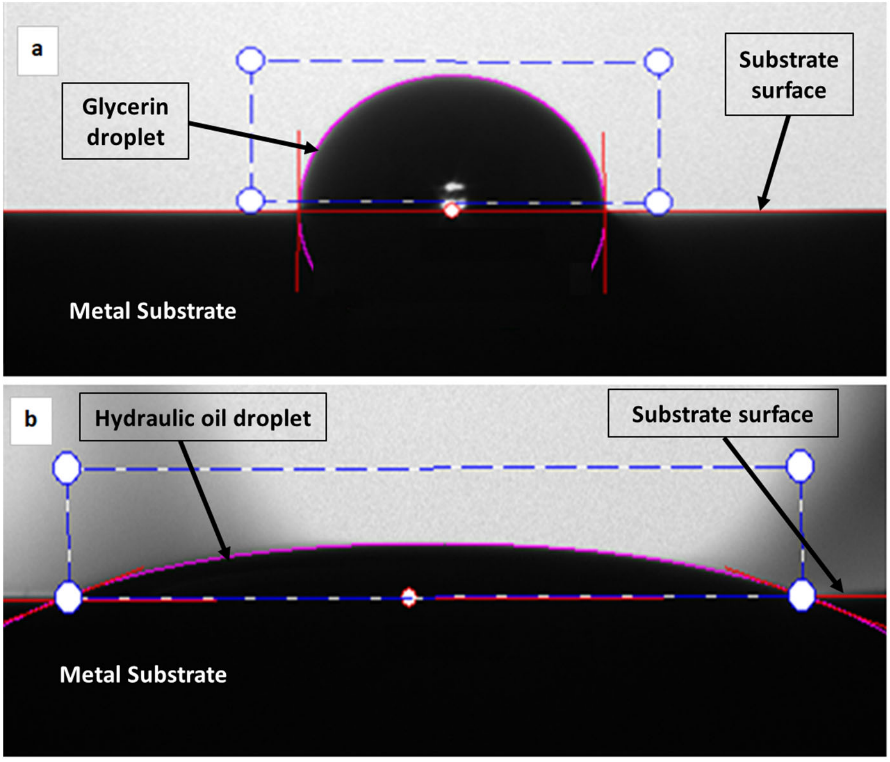

Figure 2. The silhouette of the droplets on the silver substrate ((**a**): glycerin droplet, (**b**): hydraulic oil droplet).

On the other hand, the high carbon content of oil influences its wettability behavior primarily through the nature of the carbon compounds present. Oils with a higher concentration of light hydrocarbons (92% in petroleum) tend to maintain wet conditions on surfaces, thanks to lower surface tension and apolar behavior. Moreover, we observed that apolar liquids work more similarly while polar liquids demonstrate other behaviors. The oil properties in the wetting condition affect the ability to improve and control the oil–water wetting; Buckley and Morrow [38] found that different species in the crude oil determine the wetting behavior.

In contrast to water and glycerin wetting behavior, in experiments with the different types of oil, the contact angle on metal surfaces (see Table 1) approached a lower value after only 3–4 s, demonstrating that oil has a very high speed of liquid spreading on all types of metal surfaces (Figure 2b) because of its low surface tension. The wettability of petroleum was better than that of hydraulic oil on all types of substrates, and these differences depend on the balance between adhesive forces (between the oil and the metal) and cohesive forces (within the oil).

By examining the contact angles of different oil types on metal surfaces in relation to their atomic numbers, and comparing them to distilled water and glycerin behavior, it becomes evident that the contact angle aligns with the periodicity corresponding to the substrate's atomic number. As illustrated in Figure 3, the atomic radius of the substrate can affect the contact angle value measured on its surface due to the interactions between the substrate, the liquid, and the surrounding environment, proving the difference in behavior between the polar liquids (distilled water and glycerin) and apolar liquids (hydraulic oil and petroleum). While the variations observed in the results for the relationship between oil and water contact angles and the atomic number occur because the atomic number can correlate with electronic properties (e.g., electron density), which influence surface energy, this relationship may not be linear or consistent across all metals due to differences in their crystal structure and surface chemistry. This may explain the variations in results for different metals. The atomic radius is a crucial parameter for understanding wetting behavior and surface interaction influences on contact angle for the following points:

1. Atomic Interactions: The strength and type of interactions between the liquid molecules and the solid surface could be affected by the atomic radius of the substrate. A larger atomic radius often corresponds to a larger surface area and more available interaction sites. The concept depends on the idea that as the atomic radius increases, the overall size of atoms or molecules increases, potentially offering more surface area for interactions, especially in chemical reactions, adsorption processes, or catalytic activity [39,40]. Substrates with larger atomic radii might have more surface sites capable of forming hydrogen bonds, dipole–dipole interactions, or van der Waals forces with the liquid molecules.
2. Pore size and Roughness: In porous substrates or surfaces with nanoscale roughness, the atomic radius of atoms making up a porous material can influence the overall structure of the pores, and larger atomic radii might lead to a more open structure that allows easy infiltration of the liquid, resulting in a lower contact angle. However, pore size is more directly related to the material structure (like the crystal lattice, the atom arrangement, or even the way the particles are packed) rather than only atomic radius. Pore size and surface roughness directly impact liquid infiltration and the contact angle, while a larger atomic radius can indirectly contribute to a more open structure [41,42].
3. Surface Energy and Wetting: The surface energy of a solid substrate plays a significant role in wetting behavior. If the liquid's cohesive forces are stronger than the adhesive forces between the liquid and the solid, the liquid tends to bead up and form a higher contact angle. On the other hand, if the adhesive forces are stronger, the liquid spreads out and forms a lower contact angle [43].
4. Capillary Action: The ability of a liquid to flow in a narrow area against the force of gravity is called capillary action, which can also be affected by the atomic radius. This is usually a structural effect of the material rather than a direct result of atomic size, where capillary action is influenced by the dimensions of the capillaries, which in turn can be affected by the material's atomic structure. It is determined by how atoms or molecules are arranged within the material rather than just their atomic radii, which might lead to capillaries with different dimensions. A material composed of atoms with a larger atomic radius might exhibit different pore or capillary sizes, indirectly influencing capillary action and potentially altering the contact angle [43–45].
5. Chemical Interactions: The atomic radius is often linked to the chemical properties of the substrate. Substrates with larger atomic radii might have more polarizable electrons, affecting the strength of van der Waals forces or inducing stronger dipole interactions with the liquid [46].
6. High and Low Atomic Density: Surfaces with high atomic density (Tightly Packed Atoms) are smoother and have fewer irregularities. Oil spreads more easily on such surfaces because there are fewer energy barriers, creating a more uniform interaction between the surface and the oil. This enhances the wettability of the surface by the oil. Surfaces with low atomic density (Loosely Packed Atoms) are rougher or have more gaps, which can reduce the wettability, as the oil may form patches instead of spreading uniformly [43].

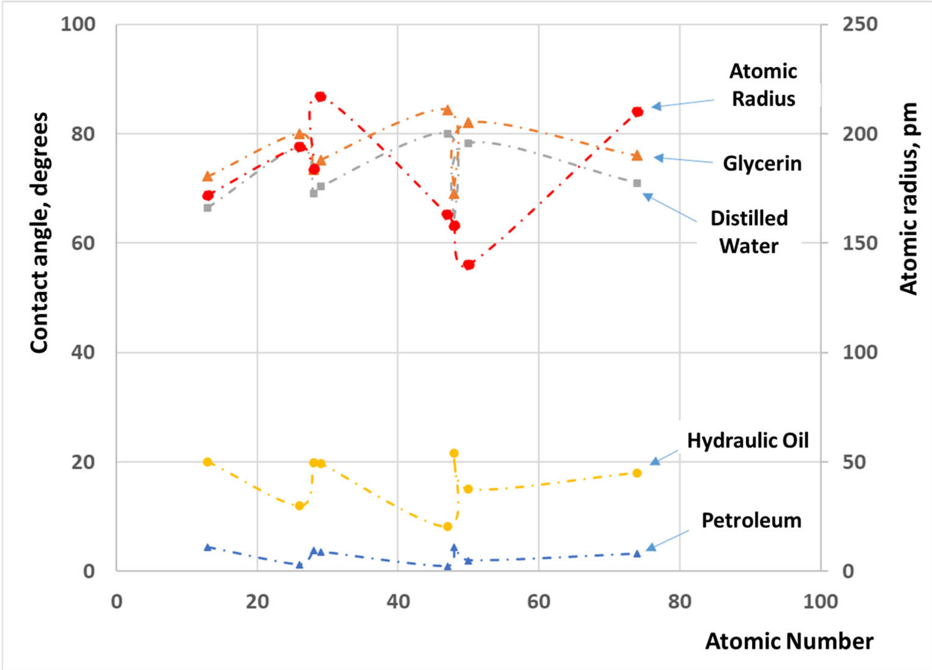

Figure 3. Measured contact angles of the liquid (oil types and distilled water) and atomic radius of the substrate as a function of the substrate atomic number.

Figure 4 shows good correlation between the cosine of the contact angles of the liquids on metal surfaces and the atomic radius of the metal substrates. It is evident that a strong correlation exists, as indicated by the high correlation coefficient R^2 for petroleum (0.91), hydraulic oil (0.88), distilled water (0.95), and glycerin (0.91). The linear relationship between the cosine of the contact angle (cosθ) and the atomic radius of a metal arises from how the atomic radius affects the surface energy and, consequently, wettability.

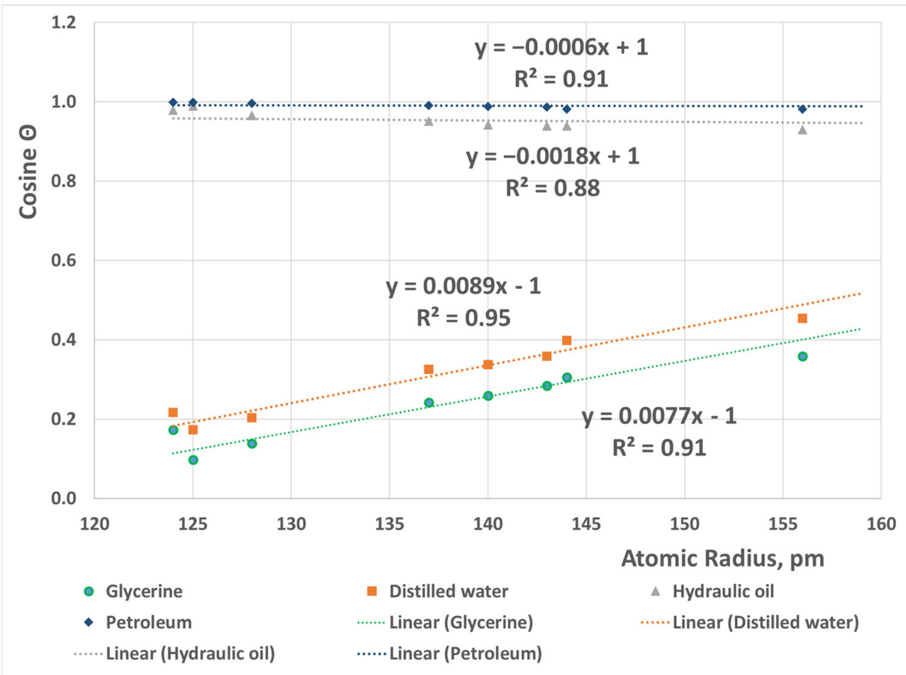

Figure 4. Cosine of the contact angle of liquids as a function of the atomic radius parameter of the substrate.

Based on our measured data and observations in wettability tests, we applied the broken bond model to describe more precisely the wettability behavior in our liquid/metal systems.

3.2. Broken Bond Model

For more accurate predictions in a specific liquid/metal system, we will turn to Becker's broken bond model [47,48] and prove the relationship between the contact angle and the atomic radius (half the bond length). In this model, the interfacial energy between two phases (A and B) can be calculated as follows:

$$\sigma_{AB} = n_{AB}\left(V_{AB} - \frac{V_{AA} + V_{BB}}{2}\right), \tag{1}$$

where n_{AB} is the number of cross bonds per unit area, and V_{ij} are the bond energies of interatomic pairs in phases A and B. Thus, for the solid–gas (SG), solid–liquid (SL), and liquid–gas (LG) interfaces, the interfacial energies are

$$\sigma_{SG} = n_{SG}\left(V_{SG} - \frac{V_{SS} + V_{GG}}{2}\right), \tag{2}$$

$$\sigma_{SL} = n_{SL}\left(V_{SL} - \frac{V_{SS} + V_{LL}}{2}\right), \tag{3}$$

$$\sigma_{LG} = n_{LG}\left(V_{LG} - \frac{V_{LL} + V_{GG}}{2}\right). \tag{4}$$

If we assume that the solid–gas (V_{SG}), liquid–gas (V_{LG}) and gas–gas (V_{GG}) pair interaction energies are negligible compared to the others, then Equations (2) and (4) are simplified as follows:

$$\sigma_{SG} = -\frac{1}{2}n_{SG}V_{SS}, \tag{5}$$

$$\sigma_{LG} = -\frac{1}{2}n_{LG}V_{LL}, \tag{6}$$

which are formulas often used for surface energies in the literature [48]. Substituting Equations (3), (5) and (6) into Young's equation, we obtain

$$cos(\Theta) = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}} = \frac{-\frac{1}{2}n_{SG}V_{SS} - n_{SL}V_{SL} + \frac{1}{2}n_{SL}V_{SS} + \frac{1}{2}n_{SL}V_{LL}}{-\frac{1}{2}n_{LL}V_{LG}}. \tag{7}$$

If we use the approximation that $n_{SL} \approx n_{LG} \approx n_{SG}$, Equation (7) takes the following form:

$$cos(\Theta) = 2\frac{V_{SL}}{V_{LL}} - 1, \tag{8}$$

Note that this equation returns the expected limiting cases, namely if the solid–liquid interaction is strong $(V_{SL} \approx V_{LL})$, then $\cos(\Theta) \approx 1$, making $\Theta \approx 0^\circ$, i.e., the liquid perfectly wets the surface; but if the solid–liquid interaction is negligible compared to the liquid–liquid interaction $(V_{SL} \ll V_{LL})$, then $\cos(\Theta) \approx -1$, i.e., $\Theta \approx 180^\circ$, i.e., the liquid does not wet the surface.

It is clear from Equation (8) that the dependence of $\cos(\Theta)$ on the atomic radius (r_a) is determined by the dependence of V_{SL} on r_a, since this varies as the substrate changes. The simplest approximation is to assume that this dependence is linear.

$$V_{SL} = \alpha r_a + \beta \tag{9}$$

where α and β are semi empirical parameters. In this case, $\cos(\Theta) \propto r_a$. Figure 4 shows that the experimental data fit very well with a linear function on the $\cos(\Theta) - r_a$ diagram.

Note that for water and glycerin $\alpha < 0$, while for petroleum and hydraulic oil $\alpha > 0$. This is probably due to the difference in the metal–liquid bond, as distilled water and glycerin are composed of polar molecules, whereas hydraulic oil and petroleum are composed of apolar molecules. It is obvious that, for example, for covalent bonds, increasing the atomic radius would result in a larger distance and a weaker bond, while for ion–dipole or dipole–diploe interactions, increasing the atomic radii would cause higher polarizability, and thus greater intermolecular attraction. The substrates with larger atomic radii might have more polarizable electrons, affecting the strength of interactions with the liquid. Since ion–dipole and dipole–dipole interactions are weak bonds, this may explain why the dependence on the radius of the substrate atoms (see Figure 4) is two orders of magnitude weaker for distilled water and glycerin than for petroleum and hydraulic oil (see the slopes of the fitted lines in Figure 4).

To verify the prediction of the result of the equation that we obtained, we used Bismuth metal as an example, wetted by the polar and apolar liquids, where the experimentally identified contact angles are $\Theta_W = 79° \pm 3°$, $\Theta_G = 83° \pm 3°$, $\Theta_H = 14° \pm 3°$, and $\Theta_P = 9° \pm 3°$ for water, glycerin, hydraulic oil, and petroleum, respectively. Using the equation While by using the equations from Figure 4, the counted contact angles are $\Theta_W = 73° \pm 3°$, $\Theta_G = 82° \pm 3°$, $\Theta_H = 17° \pm 3°$, and $\Theta_P = 10° \pm 3°$.

4. Conclusions

This study explores wettability through the examination of various liquid types: distilled water, glycerin, hydraulic oil (HME10), and petroleum, which were applied to a range of samples: Ni, Cu, Ag, Al, W, Sn, Fe, and Cd. The findings are as follows:

- The atomic radius of the substrate significantly impacts the contact angle values, and therefore the overall wetting behavior will be impacted.
- Nickel exhibits superior oil wetting, displaying consistently lower contact angles throughout the testing. This distinction can be attributed to oxide formation on the surface of the other metals, resulting in their decreased surface energy and decreased wettability.
- Glycerin and distilled water share a similar wettability pattern on identical metal surfaces, owing to their relatively high surface tensions.
- Petroleum demonstrates remarkably rapid wetting compared to glycerin and distilled water. These novel observations could find applications in oil–water separation processes in the oil industry.
- The linear relation between atomic radius and wettability was proved by Becker's broken bond model.
- An equation has been developed aiming to predict the wettability behavior of metals.

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