Determination of Thermodynamic Characteristics of Metal Surfaces under Selective Wetting Conditions

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Abstract—Surface free energy and its components for the oxidized and unoxidized metallic surfaces are determined under selective wetting conditions using test liquids and neutral hydrocarbons. A well-distinguished oleophily of the surfaces under study due to their molecular nature is established. A preliminary thermal oxidation surface does not significantly affect the surface characteristics.

INTRODUCTION

Determination of surface free energy (SFE) and its components, such as Gibbs free energy and thermodynamic work of adhesion for solids, was and still is an important step in creating polymer–metal compounds having optimal adhesion properties [1–4]. Though recently this problem was quite successfully solved for polymer surfaces using the methods of air wetting, for metal surfaces matters are complicated by the fact that metals and metal oxides are high-energy surfaces that adsorb water vapor of atmosphere and other impurities, significantly reducing the measured value of SFE. In practice, these values determined for the different methods of wetting of metal substrates are small, ~40–60 mN/m. Meanwhile, the aforementioned adsorption cannot be neglected at real values of relative air humidity of 75–85%, and it is difficult and unpromising to create special conditions to prevent it.

In recent years, a number of papers appeared on various aspects of the selective wetting [5–7]. However, some issues require clarification. Therefore, the development of methods for measurement in other environments than air, for example, in a neutral hydrocarbon, is of considerable scientific interest.

THEORY

The Young equation, which is at the basis of all methods of wetting, is known to be as follows:

$$\gamma_{23} = \gamma_{12} + \gamma_{13}\cos\theta. \quad (1)$$

It is realized also when another liquid, immiscible with the first one (the test one), is used instead of air (Fig. 1).

In Eq. (1), γ_{ij} ia the interfacial energy: subscript 1 refers to the test liquid, subscript 2 refers to the studied hard surface, and subscript 3 refers to the second liquid where the measurement is carried out. The Young–Dupre equation is written as

$$W_a = \gamma_{13}(1 + \cos\theta) \quad (2)$$

or, taking into account the Antonov rule,

$$W_a = (\gamma_1 - \gamma_3)(1 + \cos\theta). \quad (3)$$

Thus, measuring the wetting angles allows determining the experimental values of the thermodynamic work of adhesion W_a and then calculating free energy ΔG_{123} equal to it with opposite sign:

$$\Delta G_{123} = -W_a = \gamma_{12} - \gamma_{13} - \gamma_{23}. \quad (4)$$

Since finding the Lifshitz–van der Waals components and acid–base parameters (γ^{LW} and γ^{AB}), as well as acidic and basic parameters (γ^+ and γ^-), of SFE of
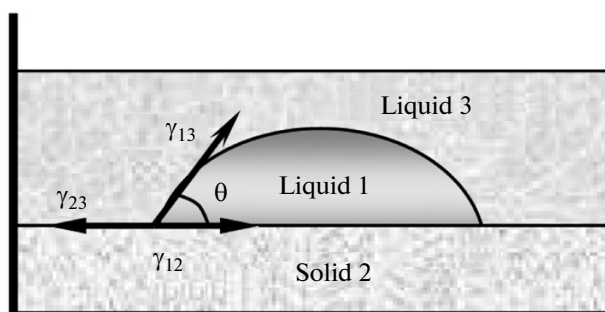

Fig. 1. Determination of the equilibrium angle under selective wetting conditions.

Table 1. Results of selective wetting of metal surfaces

Test liquid	Cosine of wetting angle for samples*				
	1	2	3	4	5
Water	−0.59	−0.52	−0.6	−0.5	−0.87
Formamide	−0.33	−0.59	−0.59	−0.25	−0.81
Glycerol	−0.70	−0.75	−0.83	−0.67	−1.0
Aqueous phenol solution	0.62	0.63	0.1	0.65	
DMSO	−0.48	−0.2	−0.52	−0.22	
DMF	0.06	−0.25	−0.31	−0.2	

* Samples: (1) steel unoxidized in hexane, (2) steel oxidized in hexane, (3) steel unoxidized in hexadecane, (4) steel oxidized in hexadecane, and (5) steel unoxidized in *o*-xylene.

the metal under study is of great interest, we use relations for the interfacial cooperation energy of liquid 1−solid 2, liquid 1−liquid 3, and liquid 3−solid 2:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} - 2\sqrt{\gamma_1^+\gamma_2^-} - 2\sqrt{\gamma_1^-\gamma_2^+}, \quad (5)$$

$$\gamma_{13} = \gamma_1 + \gamma_3 - 2\sqrt{\gamma_1^{LW}\gamma_3^{LW}} - 2\sqrt{\gamma_1^+\gamma_3^-} - 2\sqrt{\gamma_1^-\gamma_3^+}, \quad (6)$$

$$\gamma_{23} = \gamma_2 + \gamma_3 - 2\sqrt{\gamma_2^{LW}\gamma_3^{LW}} - 2\sqrt{\gamma_2^+\gamma_3^-} - 2\sqrt{\gamma_2^-\gamma_3^+}. \quad (7)$$

Combining Eqs. (4) and (5)−(7), we obtain

$$
\begin{aligned}
\Delta G_{123} = \; & \gamma_1 + \gamma_2 - (\gamma_1 + \gamma_3) - (\gamma_2 + \gamma_3) \\
& - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} - 2\sqrt{\gamma_1^+\gamma_2^-} - 2\sqrt{\gamma_1^-\gamma_2^+} \\
& + 2\sqrt{\gamma_1^{LW}\gamma_3^{LW}} + 2\sqrt{\gamma_1^+\gamma_3^-} + 2\sqrt{\gamma_1^-\gamma_3^+} \\
& + 2\sqrt{\gamma_2^{LW}\gamma_3^{LW}} + 2\sqrt{\gamma_2^+\gamma_3^-} + 2\sqrt{\gamma_2^-\gamma_3^+} \\
= \; & -2[\gamma_3 + \sqrt{\gamma_1^{LW}\gamma_2^{LW}} - \sqrt{\gamma_1^{LW}\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}\gamma_3^{LW}} \\
& - \sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+} - \sqrt{\gamma_1^+\gamma_3^-} - \sqrt{\gamma_1^-\gamma_3^+} - \sqrt{\gamma_2^+\gamma_3^-} - \sqrt{\gamma_2^-\gamma_3^+}].
\end{aligned}
\quad (8)
$$

Equation (8) may be simplified if a neutral liquid with $\gamma_3^+ = \gamma_3^- = 0$ is chosen as liquid 3. Then,

$$
\begin{aligned}
\Delta G_{123} = \; & -2[\gamma_3^{LW} + \sqrt{\gamma_1^{LW}\gamma_2^{LW}} - \sqrt{\gamma_1^{LW}\gamma_3^{LW}} \\
& - \sqrt{\gamma_2^{LW}\gamma_3^{LW}} + \sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}].
\end{aligned}
\quad (9)
$$

In the resulting equation (9), the values γ_3^{LW}, γ_1^{LW}, γ_1^+ and γ_1^- are known, while the Lifshitz−van der Waals component γ_2^{LW} and acidic γ_2^+ and basic γ_2^- SFE parameters of solid are unknown. After substituting the known values, Eq. (9) is converted into a linear one with three unknowns. From the experiment, $\Delta G_{123} = -W_a$ is found. In constructing the system of at least three such equations for the different test liquids, it is easy to find the final values γ_2^{LW}, γ_2^+, and γ_2^- for the "pure" metal surfaces.

EXPERIMENTAL

Measurements of wetting angles were performed on a CM-8 cathetometer in a medium of hexane, hexadecane and *o*-xylene. As a test liquid, we used twice-distilled water, formamide, glycerol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and 88% aqueous phenol solution. Components and SFE parameters of test liquids were taken from [4].

Steel plate St3 was used as a metal support. Plates were treated with sandpaper to purity class 10, washed with carbon tetrachloride. and immediately placed in a cuvette of optical glass with a neutral hydrocarbon (unoxidized steel). To obtain an oxide film, the plates prepared using the method described above were incubated in an oven at 190°C for 2 h.

Drops of test liquids were applied using a syringe with a needle sawn at a right angle.

As a medium for measurement, we used neutral hydrocarbons with different SFE: *n*-hexane (18.43), *n*-hexadecane (27.47), and *o*-xylene (30.03) [8]. For each of them, $\gamma_3 = \gamma_3^{LW}$. Both a nonpolar hydrocarbon and test liquid can wet the test surface, so between them, in each case, there is concurrence. The drop shape is determined by the balance of intermolecular interactions of certain liquids and liquids with solids. It can be said of the liquid wetting the surface better that it has greater selective wetting with respect to the surface. This quality belongs to a liquid the polarity of which is closer to the polarity of the solid, and the surface energy of the system is reduced by a large amount when it flows.

The surface is considered as hydrophilic if the water wets it better than the nonpolar hydrocarbon (the angle cosine is less than 90°). Otherwise, the surface is oleophilic or hydrophobic. According to Eq. (1), this takes place at $\gamma_{12} > \gamma_{23}$, i.e., where the interfacial energy of the metal−water interaction is higher than that of metal−hydrocarbon. The measured values of wetting angles of metallic substrates using various test liquids in hydrocarbons are shown in Table 1.

Unfortunately, not all the used test liquids form drops in *o*-xylene due to possible formation of donor−

Table 2. Calculation results of SFE of metals

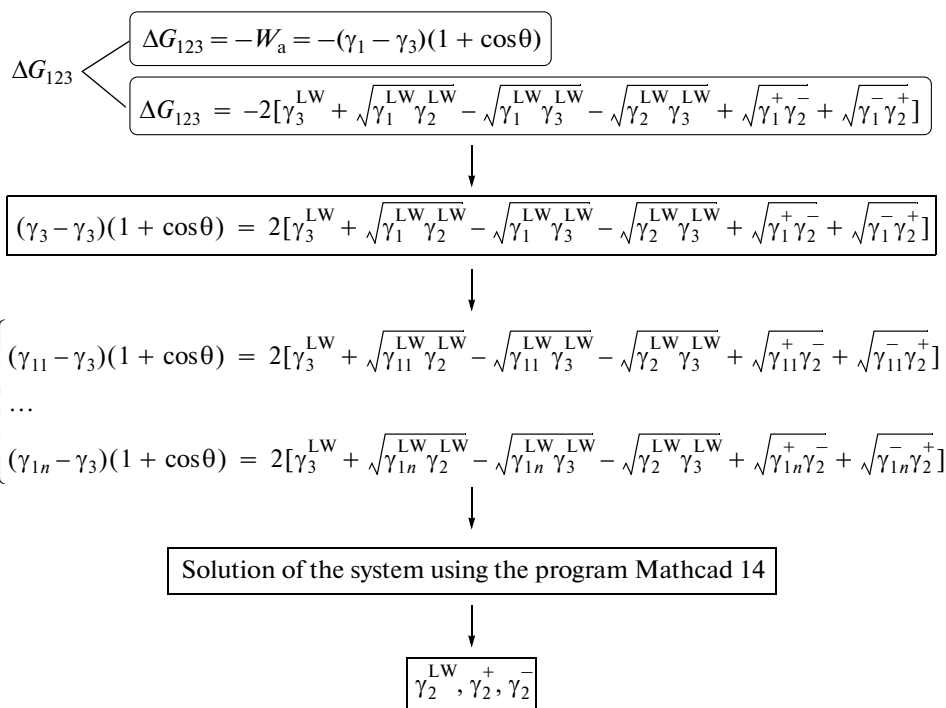| Sample entry	SFE components				
	γ_S^{LW}	γ_S^{AB}	γ_S^+	γ_S^-	γ_2
1	93.32	0.56	0.21	0.38	93.88
2	90.5	0.47	0.46	0.12	90.97
3	33.1	0.61	0.26	0.36	33.71
4	48.52	0.92	0.13	1.58	49.44

acceptor complexes between *o*-xylene and solvent, such as DMF and DMSO [5].

Analysis of the results proves the oleophilicity of the studied surfaces, regardless of the degree of oxidation: the cosine of the wetting angle with water is negative in all cases. Consequently, neutral hydrocarbons possess a large selective wetting of steel and its oxides. This effect increases with an increase in the surface tension of neutral hydrocarbon (Table 1), as well as in cases in which formamide or glycerol are taken as test liquids. The liquid is known to wet a solid surface better if the interaction between its molecules is small;

therefore, nonpolar liquids with a low surface tension wet a metal surface better than the test one.

The aim of the study was to determine γ_2^{LW}, γ_2^+, and γ_2^- for metal surfaces. For this purpose, using the Mathcad 14 program, we solved system of linear equations (9). The algorithm to find solutions is given in the scheme of Fig. 2. The calculation results are presented in Table 2.

Table 2 shows a strong dependence of the obtained values on the hydrocarbon used. In addition, there is weakly expressed polarity of metal substrates, which is

$$\Delta G_{123} \begin{cases} \Delta G_{123} = -W_a = -(\gamma_1 - \gamma_3)(1 + \cos\theta) \\ \Delta G_{123} = -2[\gamma_3^{LW} + \sqrt{\gamma_1^{LW}\gamma_2^{LW}} - \sqrt{\gamma_1^{LW}\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}\gamma_3^{LW}} + \sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}] \end{cases}$$

$$(\gamma_3 - \gamma_3)(1 + \cos\theta) = 2[\gamma_3^{LW} + \sqrt{\gamma_1^{LW}\gamma_2^{LW}} - \sqrt{\gamma_1^{LW}\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}\gamma_3^{LW}} + \sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}]$$

$$\begin{cases} (\gamma_{11} - \gamma_3)(1 + \cos\theta) = 2[\gamma_3^{LW} + \sqrt{\gamma_{11}^{LW}\gamma_2^{LW}} - \sqrt{\gamma_{11}^{LW}\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}\gamma_3^{LW}} + \sqrt{\gamma_{11}^+\gamma_2^-} + \sqrt{\gamma_{11}^-\gamma_2^+}] \\ \dots \\ (\gamma_{1n} - \gamma_3)(1 + \cos\theta) = 2[\gamma_3^{LW} + \sqrt{\gamma_{1n}^{LW}\gamma_2^{LW}} - \sqrt{\gamma_{1n}^{LW}\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}\gamma_3^{LW}} + \sqrt{\gamma_{1n}^+\gamma_2^-} + \sqrt{\gamma_{1n}^-\gamma_2^+}] \end{cases}$$

Solution of the system using the program Mathcad 14

$$\gamma_2^{LW}, \gamma_2^+, \gamma_2^-$$

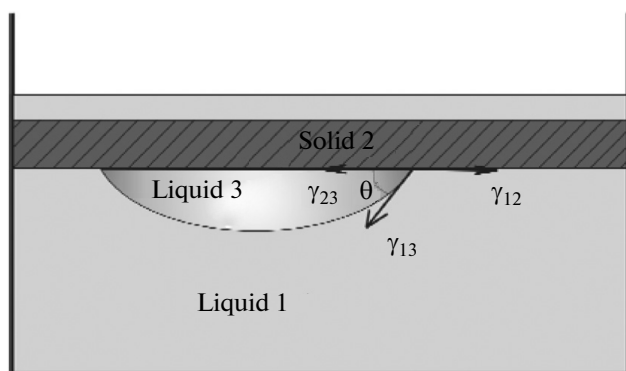**Fig. 2.** Algorithm to obtain the components and parameters of SFE of a solid.

Fig. 3. Scheme of "inverse" of the experiment in a selective wetting.

evidenced by the low value (in all cases) of the acid–base component of SFE. However, measurements conducted in hexane give higher SFE of metals than in air [9, 10].

Determining the values of selective wetting of metals is particularly difficult. According to P.A. Rehbinder, metals are hydrophobic. Rehbinder explains that this is due to their metal homopolar lattice (atomic–electronic), which differs from the typical heteropolar lattice (ionic) of hydrophilic compounds. However, he noted that the metal surface in water, and not only in air, is always covered with an invisible, very thin thinnest oxide film that improves its hydrophilicity.

To interpret the obtained values, we performed a "reverse" experiment, which took the form of measurement of wetting angles of metal with neutral hydrocarbons in water. Since the density of water is higher than that of hexane and hexadecane, the scheme of this experiment is presented in Fig. 3.

Drops of hydrocarbon were deposited using syringe a with a curved needle on the metal surface. The average cosine of the wetting angle of unoxidized steel was 0.69 with hexane and 0.8 with hexadecane. If these values were to be measured in the "direct" experiment (i.e., the wetting angle were to be measured not from the side of the test liquid, but from the side of hydrocarbon), we would obtain a cosine of the wetting angle of the nonoxidized steel equal to 0.59 for hexane and 0.6 for hexadecane. Correspondingly, the cosines of wetting angles for the same samples were −0.59 and −0.6 in the water in the "direct" experiment and −0.69 and −0.8 in the "reverse" one. There exists a discrepancy, which Rehbinder's classical studies referred to as the "static wetting hysteresis." If the cosine of the wetting angle of the metal substrate with water (or other test liquid) in the medium of neutral hydrocarbon is denoted as $\cos\theta_{13}$, while the same angle formed by hydrocarbon in the test liquid medium and measured from the side of water is $\cos\theta_{31}$, the numer-

ical expression for static hysteresis is the difference $\Delta = \cos\theta_{31} - \cos\theta_{13}$. In our case, the hysteresis is not so significant: 0.1 for the hexane–water system and 0.2 for the water–hexadecane system. This static hysteresis brought about by the sequence of depositing the drops is always present in the selective wetting.

Thermal treatment of the substrates practically does not increase their hydrophilicity and, hence, the polarity. The wetting angle decreases by only 5°–7°. This may be due to side atmospheric adsorption of organic substances during cooling of the substrates. In further research, it will be necessary to minimize these effects.

The dependence of the obtained values of hydrocarbon surface tension makes it possible to determine the adjusted value of the SFE of metals and its components through extrapolation at expanding the range of hydrocarbons with differing surface tension.

The method of selective wetting can be applied to monitor the adsorption processes and the formation of thin oxide films on the metal surfaces, which is important in the study of adhesive interaction in polymers and metals.

CONCLUSIONS

(1) The values of the components and parameters of SFE depend on the hydrocarbon: the lower its surface tension, the higher the obtained value of the total SFE of metal surface.

(2) The increase in the surface hydrophilicity due to oxidation appears to be insignificant, which may be due to side atmospheric adsorption during cooling the substrates.

(3) The method of selective wetting makes it possible to measure the wetting angles of neutral hydrocarbons, which flow completely over the surface in air, on metal substrates.

(4) The proposed approach is an interesting and promising area of research, because the determination that is used of wetting angles in the air does not characterize the molecular nature of the metal surface to a sufficient degree.

ACKNOWLEDGMENTS

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