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## Analysis of the results of surface free energy measurement of Ti6Al4V by different methods

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### Abstract

Surface Free Energy (SFE) of solids should be calculated using theoretical models. The contact angle (CA) measurement on a surface is considered the most practical way to obtain the SFE. The results of five methods based in the models are compared: the method of Zisman (ZI), the geometric mean (GM), the harmonic mean (HM), the Lifshitz-van der Waals / Acid-Base (LW/AB) and the equation of state (ES). The SFE calculated with GM, HM and LW/AB methods change with the amount and type of liquid used, however, when water, glycerol and dimethyl sulfoxide are used together the SFE and its dispersive and polar components are similar in value for the three methods. In the case of the ES model the values of SFE change with the liquid used; finally using the ZI method the SFE values are 20% lower than the values of SFE obtained with the other methods.

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*Keywords:* surface free energy; sessile drop method; theoretical models

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### 1. Introduction

The surface free energy (SFE) is a characteristic parameter of a material strongly associated to the state of equilibrium of the atoms in the surface and its value depends on the nature and the aggregate state of the material. The SFE is defined as the work necessary to apply to produce a new surface of material, and is given as energy/surface area; in the MKS system the units are  $\text{mJ}/\text{m}^2$  [Rudawska et al. (2009)]. Many of the interactions with the surrounding media depend on the value of the SFE, i.e. adsorption, wetting and adhesion; therefore, reliable

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methods for determining the precise SFE values are required for predicting the degree and type of interactions [Roy et al. (2007), Gindl et al. (2001)].

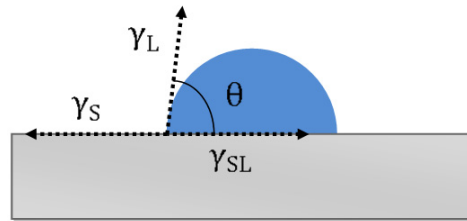


Fig. 1. Schematic of a liquid drop showing the quantities in Young's equation.

Since direct measurement of the SFE in solid is not possible, the determination is carried out using indirect methods which rely on different theoretical approaches. However, there is no agreement on which is the most reliable method. In general the calculation of SFE is based on measurements of contact angle of liquids deposited on the solid surface as shown in Figure 1; this value is used in the well known Young equation [Gindl et al. (2001), Zhao et al. (2004), Żenkiewicz (2007)]:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \quad (1)$$

Where  $\gamma_L$  and  $\gamma_S$  are the SFE of the liquid and solid respectively,  $\gamma_{SL}$  is the solid-liquid interfacial energy and  $\theta$  is the contact angle. Both,  $\gamma_L$  (experimental surface tension) and  $\theta$  can be easily determined, however the value of  $\gamma_{SL}$  must be known to calculate  $\gamma_S$ . There are different theoretical models to calculate  $\gamma_{SL}$  and  $\gamma_S$ , five of them are used in the present report as follows: the Zisman method [Zisman (1963)], the geometrical mean method [Owens et al. (1969)], the harmonic mean method [Wu (1971)], the Lifshitz-van der Waals/Acid-Base method [Van Oss et al. (1988)] and the method based on the equation of state [Kwok et al. (2000)]. In the last four methods the value of  $\gamma_{SL}$  is estimated by means of molecular interactions considerations and assuming certain relations among  $\gamma_L$ ,  $\gamma_S$  and  $\gamma_{SL}$ ; the Zisman method employ the concept of critical surface energy instead of the Young equation.

In the present report the five methods are employed to estimate the SFE of smooth surfaces of titanium dioxide films formed on Ti6Al4V alloys and using different liquids in order to compare the results and analyze which is the easiest and most reliable method.

## 2. Methodology

### 2.1. Materials

The substrates were rectangular plates 1 cm x 2 cm of Ti6Al4V alloy, which were first mechanically polished with SiC abrasive paper of granulometry from 220 to 1500, then with diamond paste of 1  $\mu\text{m}$  lubricated with ethylene glycol, and finally with a chemical-mechanical method using a silicon suspension of particles 0,02  $\mu\text{m}$  in size in  $\text{H}_2\text{O}_2$ . The final polishing step produces a  $\text{TiO}_2$  film of approximately 10 nm [Bakir (2012)]. Three samples were obtained.

Table 1. Data of surface tension and components of the test liquids used in this work ( $\text{mJ}/\text{m}^2$ ) [Zhao et al. (2004), Kwok (1999)]

Liquid	$\gamma_L$	$\gamma_L^d$ or $\gamma_L^{LW}$	$\gamma_L^p$ or $\gamma_L^{AB}$	$\gamma_L^+$	$\gamma_L^-$	Polarity [ $\gamma_L^p/\gamma_L^d$ ]
Water (W)	72.8	21.8	51.0	25.5	25.5	2.3
Glycerol (G)	64.0	34.0	30.0	3.92	57.4	0.9
Ethylene glycol (E)	48.0	29.0	19.0	1.92	47.0	0.7
Dimethyl sulfoxide (D)	44.0	36.0	8.0	0.50	32.0	0.2

## 2.2. Roughness

The surface roughness was determined employing a profilometer with a resolution of 10 nm and with a RC phase contrast filter with a cut-off of 0,8 mm along a length  $L = 4$  mm. The reported value is the average of 5 readings corresponding to different places and in different directions.

## 2.3. Contact Angle

The contact angle was measured using the sessile drop method and a goniometer built for the present research which was previously and properly calibrated, which consisted on acquiring pictures of each drop and processing the pictures with the software ImageJ [Rasband (1997–2014)]. The drop volume varied between 3 to 5 mm<sup>3</sup>. The contact angle in each drop is the average value of the angle measured at the left and right sides of the drop picture. Before depositing a drop, the film surface is washed with detergent, rinsed with deionized water and then with ethanol and finally dried with hot air. The contact angles of 5 drops were measured at room temperature ( $25 \pm 3$  °C).

## 2.4. Surface Free Energy

### 2.4.1. The Zisman Method

The Zisman method introduces the concept of critical surface energy ( $\gamma_c$ ) which is defined as the surface free energy of a liquid that completely wets a surface, that is, the contact angle is zero and  $\cos \theta = 1$ . The value of  $\gamma_c$  is obtained by measuring the contact angle of a number of different liquids on the same surface, plotting the points in  $\cos \theta_L$  vs  $\gamma_L$  axes, extrapolating the fitted curve to the value of  $\cos \theta = 1$  and obtaining the value  $\gamma_c$  from the abscissa. The value of  $\gamma_c$  is related through empirical relations developed by Zisman [Zisman (1963)] with the surface free energy of the film.

### 2.4.2. Methods of the Geometrical Mean (GM) and Harmonic Mean (HM)

The HM and GM models are based on the assumption that the intermolecular interactions between two substances have two main components; the dispersive or London component and the polar component due to the contributions given by the Keesom and the Debye forces. Therefore the SFE( $\gamma$ ) arises from these interactions contributions as the sum of two components, the dispersive ( $\gamma^d$ ) and the polar components ( $\gamma^p$ ) as [Gindl et al. (2001), Zhao et al. (2004), Wu (1971)]:

$$\gamma_i = \gamma_i^d + \gamma_i^p \quad (2)$$

where  $i$  stands for the  $i$ -substance or material, in our case liquid or solid.

According to the GM method the interfacial solid/liquid energy can be evaluated using the following equation [Owens et al. (1969)]:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2 \left( \sqrt{\gamma_S^d \cdot \gamma_L^d} + \sqrt{\gamma_S^p \cdot \gamma_L^p} \right) \quad (3)$$

which combined with the Young equation results in:

$$\gamma_L (1 + \cos \theta) = 2 \sqrt{\gamma_S^d \cdot \gamma_L^d} + 2 \sqrt{\gamma_S^p \cdot \gamma_L^p} \quad (4)$$

In order to calculate  $\gamma_S$  by equation (2), the values of  $\gamma_i^d$  and  $\gamma_i^p$  are necessary. In the case of the GM method and in order to calculate  $\gamma_S^d$  and  $\gamma_S^p$ , equation 4 is linearized as:

$$\frac{0.5 \gamma_L (1 + \cos \theta)}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p} \left( \frac{\gamma_L^p}{\gamma_L^d} \right)^{1/2} + \sqrt{\gamma_S^d} \quad (5)$$

where  $\sqrt{\gamma_S^p}$  and  $\sqrt{\gamma_S^d}$  are the slope and the ordinate to the origin respectively in a linear plot, where the variables  $0.5 \gamma_L (1 + \cos \theta) / \sqrt{\gamma_L^d}$  and  $\sqrt{\gamma_L^p / \gamma_L^d}$  are the ordinate and the abscissa, respectively. The minimum number of points to obtain a solution is two, which is obtained using only two different liquids. If more than two liquids are used. The points are fitted by a linear fitting method.

On the other hand, the solid/liquid interfacial energy by the HM method is given by [Wu (1971)]:

$$\gamma_{SL} = \gamma_S + \gamma_L - \frac{4\gamma_S^d\gamma_L^d}{\gamma_S^d + \gamma_L^d} - \frac{4\gamma_S^p\gamma_L^p}{\gamma_S^p + \gamma_L^p} \quad (6)$$

which again, combined with the Young equation results in the following equation:

$$\gamma_L(1 + \cos \theta) = \frac{4\gamma_S^d\gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{4\gamma_S^p\gamma_L^p}{\gamma_S^p + \gamma_L^p} \quad (7)$$

In the case of the HM method it is first noted that equation 7 can be written as:

$$\gamma_L(1 + \cos \theta) = f(\gamma_S^d, \gamma_S^p, \gamma_L^d, \gamma_L^p) \quad (8)$$

which shows that there are six unknown parameters  $\gamma_L, \theta, \gamma_S^d, \gamma_S^p, \gamma_L^d, \gamma_L^p$ . If the contact angle  $\theta_i$  of at least two liquids of known values  $\gamma_L, \gamma_L^d, \gamma_L^p$  are measured and each set of values  $\theta_i, \gamma_{Li}, \gamma_{Li}^d$  and  $\gamma_{Li}^p$  is used in equation 8, a set of two non-linear equations with  $\gamma_S^d$  and  $\gamma_S^p$  as unknown is obtained. This set can be solved for  $\gamma_S^d$  and  $\gamma_S^p$  by any numerical method for non-linear equations, and thus  $\gamma_S = \gamma_S^d + \gamma_S^p$ .

In the literature it is recommended to use one liquid with the polar component larger than the dispersive component and another liquid with the opposite situation [Żenkiewicz (2007)].

The values of  $\gamma_S^d$  and  $\gamma_S^p$  can also be calculated using several pairs of different liquids. In such case the result may not be unique if the above method is employed for each pair of liquids. If more than two liquids are used, the experimental points and known parameters are used in equation 7 (or symbolically equation 8), to obtain equal number of point for equation 7 with unknowns  $\gamma_S^d$  and  $\gamma_S^p$ . The set of points are used to obtain the best non-linear fitting using  $\gamma_S^d$  and  $\gamma_S^p$  as the fitting variables and  $\gamma_L(1 + \cos \theta), \gamma_L^d$  and  $\gamma_L^p$  as the experimental points to be fitted in a 3D plot.

#### 2.4.3. Lifshitz-van der Waals / Acid-Base (LW/AB)

In the LW/AB method the SFE is assumed to be composed of two main contributions, a non-polar component  $\gamma_i^{LW}$  due to Lifshitz-van der Waals, similar to the dispersive component defined above,  $\gamma_i^d$ ; and an acid-base component due to Lewis,  $\gamma_i^{AB}$ , similar to the polar component mentioned before,  $\gamma_i^p$ ; therefore, for substrate  $i$ , the SFE is written as:

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (9)$$

the acid-base component is in turn composed of two contributions; one from electron donors  $\gamma_i^-$  and another from electron acceptors  $\gamma_i^+$ . In this particular case this component is calculated as:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^- \gamma_i^+} \quad (10)$$

The solid-liquid interface energy is obtained as:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} + \sqrt{\gamma_S^+ \cdot \gamma_L^-} + \sqrt{\gamma_S^- \cdot \gamma_L^+}) \quad (11)$$

combining equations 1 with the Young equation it is obtained that:

$$\gamma_L(1 + \cos \theta) = 2(\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} + \sqrt{\gamma_S^+ \cdot \gamma_L^-} + \sqrt{\gamma_S^- \cdot \gamma_L^+}) \quad (12)$$

The calculations of the SFE of a solid using this method requires the values of the components  $\gamma_S^{LW}$  and  $\gamma_S^{AB}$ , which in turn requires to determine the values  $\gamma_S^-$  and  $\gamma_S^+$ , that is three components  $\gamma_S^{LW}, \gamma_S^-$  and  $\gamma_S^+$ . The three components appear in equation 11, together with  $\gamma_L^{LW}, \gamma_L^-$  and  $\gamma_L^+$  and  $\cos \theta$ . Therefore the three unknowns could be determined by obtaining a system of three equations using at least three liquids with known values of  $\gamma_L^{LW}, \gamma_L^-$  and  $\gamma_L^+$  and measuring the CA, for the same three liquids [Van Oss et al. (1988)].

In order to simplify the calculation, equation 12 is linearized as a function of the new variables;  $\sqrt{\gamma_L^{LW}}, \sqrt{\gamma_L^-}$  and  $\sqrt{\gamma_L^+}$  as follows:

$$\gamma_L(1 + \cos \theta_i) = 2\sqrt{\gamma_S^{LW}} \cdot \sqrt{\gamma_{Li}^{LW}} + 2\sqrt{\gamma_S^+} \cdot \sqrt{\gamma_{Li}^-} + 2\sqrt{\gamma_S^-} \cdot \sqrt{\gamma_{Li}^+} \quad (13)$$

In the case that the minimum of three liquids is used, a set of three linear equations with the above variables are obtained and solved. In the case that more than three liquids are used a numerical linear fitting is performed in order to obtain the best solution as described before.

#### 2.4.4. Equation of State (ES)

Neuman and Kwok (1999, 2000) propose the following equation for the interfacial solid-liquid energy:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S\gamma_L}[1 - \beta_1(\gamma_L - \gamma_S)^2] \tag{14}$$

which combined with the Young equation gives:

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S\gamma_L}[1 - \beta_1(\gamma_L - \gamma_S)^2] \tag{15}$$

where  $\beta_1 = 0.0001057 (m/mN)^2$  [Kwok et al. (2000)].

Equation 15 permits to evaluate the SFE of the solid ( $\gamma_S$ ), from only one contact angle measurement of a liquid with known surface tension  $\gamma_L$ . However, the method does not include the dispersive and polar components of the SFE which is important in some cases.

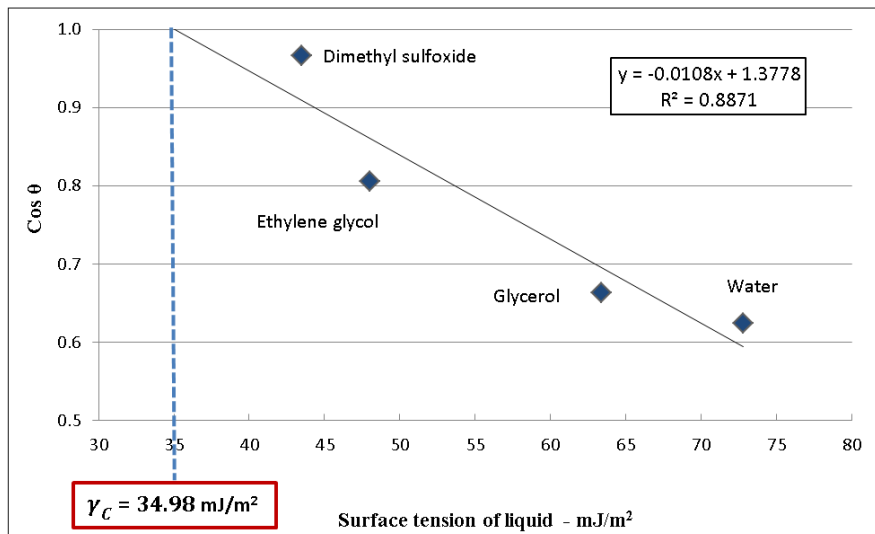


Fig. 2. Zisman Plot for sample 1 using the four liquids.

### 3. Results and Discussion

#### 3.1. Contact Angle measurement and Roughness

The contact angle of four different liquids were measured; deionized water (W), which has a predominant polar component over the dispersive component; glycerol (G) and ethylene glycol (E), both with a dispersive component slightly larger than the polar component, and finally dimethyl sulfoxide (D) with a predominant dispersive component over the polar component (see Table 1). The contact angles measured for the four liquids are listed in Table 2. The results were obtained measuring the CA for five drops in each of the three samples and show a very small standard deviation between 0.5 to 2 degrees for each sample and also a small deviation among the three samples for each liquid.

The average roughness determined in the oxidized Ti6Al4V sample surface was  $Ra = 39 \pm 10 \text{ nm}$ .

Table 2 – Measured contact angles for various liquids (in degrees).

Liquid	sample 1		sample 2		sample 3		All samples	
	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD
Water (W)	51.4	1.1	49.9	1.2	51.7	2.0	51.0	1.6
Glycerol (G)	36.3	0.5	34.9	1.3	34.7	1.5	35.2	1.3
Ethylene glycol (E)	48.5	1.0	47.3	1.2	47.6	1.9	47.8	1.4
Dimethyl sulfoxide (D)	15.5	0.9	14.9	0.5	15.1	0.8	15.2	0.7

$\bar{X}$  = mean value    SD = standard deviation

### 3.2. Surface Free Energy

#### 3.2.1. The Zisman Method (ZI)

The contact angles measured for the four liquids are plotted against the surface tension of the liquids as shown in Figure 2 for sample 1. Then a linear fitting is performed which is shown as the straight line in the figure. The extrapolation and intersection of the line at the ordinate value of  $\cos \theta = 1$  results in a value of  $\gamma_c$ , which for sample 1 is 34.98 mJ/m<sup>2</sup>. Repeating the same procedure for samples 2 and 3 results in  $\gamma_c$  values of 35.35 mJ/m<sup>2</sup> and 36.07 mJ/m<sup>2</sup>, respectively. It is noted the good reproducibility of the results with a spread of less than 3 %.

#### 3.2.2. Geometric Mean Method (GM)

The contact angles measured for each of the four liquids were combined taking the CA of 4 liquids, 3 liquids and 2 liquids at a time. In such case the number of combinations was 1, 4 and 6, respectively. In each case, equation 5 was used to obtain the best fit by the least square method. In the first case where four liquids were used, the linear fitting is shown in Figure 3(a) for sample 1 in which the slope is  $\gamma_s^p$  and the ordinate to the origin is  $\gamma_s^d$ . The results of the linear fitting for the three samples give an average of  $\gamma_s^d = 17.1 \pm 0.6$  mJ/m<sup>2</sup> and  $\gamma_s^p = 30.2 \pm 1.1$  mJ/m<sup>2</sup> and are listed in Table 3, for comparison purposes in the WEGD line.

Table 3. Surface free energy (mJ/m<sup>2</sup>) of a TiO<sub>2</sub>, calculated with the different methods using different combinations of liquids

<i>Geometric mean method</i>				
Liquids	$\gamma_s^d$	$\gamma_s^p$	$\gamma_s$	$\gamma_s^p/\gamma_s$
WEGD	17.1 ± 0.6	30.2 ± 1.1	47.3 ± 0.6	0.64
WEG	11.0 ± 0.8	37.7 ± 1.6	48.8 ± 0.9	0.77
WED	17.3 ± 0.5	30.1 ± 1.1	47.4 ± 0.6	0.64
EGD	29.1 ± 0.5	13.3 ± 0.8	42.5 ± 0.3	0.31
WGD	19.5 ± 0.5	28.8 ± 1.1	48.3 ± 0.6	0.60
WD	21.2 ± 0.4	28.0 ± 1.0	49.2 ± 0.6	0.57
WG	14.4 ± 0.8	34.0 ± 1.4	48.3 ± 0.8	0.70
WE	8.5 ± 0.7	41.0 ± 1.8	49.5 ± 1.1	0.83
DG	26.3 ± 0.5	18.0 ± 0.9	44.3 ± 0.4	0.41
DE	34.5 ± 0.6	7.5 ± 0.6	42.0 ± 0.1	0.18
GE*	-	-	-	-
<i>Harmonic mean method</i>				
Liquids	$\gamma_s^d$	$\gamma_s^p$	$\gamma_s$	$\gamma_s^p/\gamma_s$
WEGD	22.3 ± 0.2	26.7 ± 0.6	49.0 ± 0.5	0.54
WEG	14.4 ± 0.4	35.9 ± 0.9	50.3 ± 0.7	0.71
WED	23.0 ± 0.2	27.2 ± 0.6	50.2 ± 0.5	0.54
EGD	29.0 ± 0.1	15.6 ± 0.4	44.6 ± 0.3	0.35
WGD	24.6 ± 0.2	26.0 ± 0.6	50.7 ± 0.5	0.51
WD	25.8 ± 0.1	27.5 ± 0.6	53.2 ± 0.5	0.52
WG	17.5 ± 0.4	32.8 ± 0.8	50.3 ± 0.6	0.65
WE	13.7 ± 0.3	36.4 ± 0.9	50.1 ± 0.7	0.73
DG	28.3 ± 0.1	17.4 ± 0.4	45.6 ± 0.3	0.38
DE	32.3 ± 0.2	9.9 ± 0.4	42.2 ± 0.1	0.23
GE*	-	-	-	-
<i>Lifshitz-van der Waals/ Acid-Base method</i>				
Liquids	$\gamma_s^d$	$\gamma_s^p$	$\gamma_s$	$\gamma_s^p/\gamma_s$
WEGD	26.9 ± 0.9	15.7 ± 1.1	42.7 ± 0.2	0.37
WEG*	-	-	-	-
WED	39.1 ± 1.2	3.4 ± 1.2	42.5 ± 0.2	0.08
EGD*	-	-	-	-
WGD	20.5 ± 0.8	23.4 ± 1.1	43.9 ± 0.4	0.53

Ref: W: Water – E: Ethylene glycol – G: Glycerol – D: Dimethyl sulfoxide  
\*result without physical meaning

The fitting process is repeated for 4 combinations of the CA for 3 liquids and 6 combinations of 2 liquids and the results for each of the three samples are averaged and listed in Table 3. In the Table the value of  $\gamma_s$  obtained for each

case is also listed, showing a dispersion among the values for all the combinations, which is larger than the error for each combination of liquids in the results. In particular the large dispersion of values is observed for each component  $\gamma_S^d$  and  $\gamma_S^p$ , however it, results in similar values of  $\gamma_S$ . In the case of  $\gamma_S^d$ , the values range from 8.5 to 34.5 mJ/m<sup>2</sup> whereas for  $\gamma_S^p$  the range is even larger from 7.5 to 41.0 mJ/m<sup>2</sup>. The ratio  $\gamma_S^p/\gamma_S$  for the polar component contribution to the total  $\gamma_S$  is listed in the last column of Table 3 and it ranges from 18 % to 83 % of the total  $\gamma_S$ . This ratio is ordered in increasing values and plotted, in Figure 4.

It is observed that the more similar ratios or contributions of the  $\gamma_S^p$  component correspond to the combinations of liquids WD, WGD, WED and WEGD. Moreover, for all combinations, the  $\gamma_S$  calculated have values from 47.3 to 49.2 mJ/m<sup>2</sup>. Which are very close compared to the other combinations. It is noted that in these four combinations water and dimethyl sulfoxide (WD) are always present. The better regular behavior of this pair can also be observed when the values of  $\gamma_S^p/\gamma_S$  are compared among all the possible combinations of liquids in which all possible pairs of liquids are always present, regardless of the total number of liquids. The results are shown in Figure 5(a) in which the bar is the average of all the cases where that pair is present. The bars are ordered in decreasing values of dispersion in the results as indicated by each vertical segment at the top of the bar.

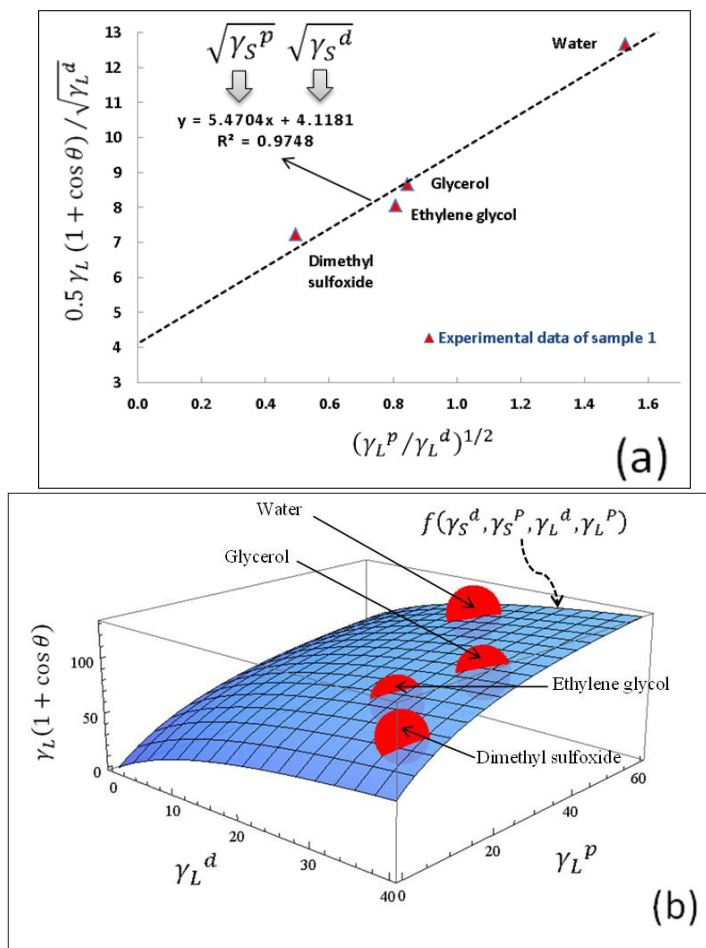


Fig. 3. Geometric mean method: linear fitting of the experimental data of sample 1 using the four liquids (a). Harmonic mean method: non-linear fitting of the experimental data of sample 1 using the four liquids (b).

It is observed that the least dispersion corresponds to those combinations of liquids which always include water and dimethyl sulfoxide, and the worst combinations are those which always include ethylene glycol and glycerol (E-G). In addition, in Figure 5(b) the  $\gamma_S$  for all the same groups of the six combinations of two liquids included in all the

possible combinations are shown. It is observed that the measurement in which WD, WG and WE are included, regardless of the number of liquids employed in the calculations, give similar values of  $\gamma_S$ , of around  $48 \text{ mJ/m}^2$ , and the smallest dispersion with respect to the other three cases.

### 3.2.3. Harmonic Mean Method (HM)

As in the GM method the same set of combinations of liquids were used; 1 with 4 liquids, 4 with 3 liquids and 6 with 2 liquids. The contact angle measured for each liquid as well as the values of the following parameter:  $\gamma_L^d$  and  $\gamma_L^p$  are employed in equation 7 in order to perform the different non-linear fittings by the least square method. The results for sample 1 are shown in Figure 3(b) for the four liquids; and in Table 3 for all the cases in which the reported values are the average for the three samples. In Figure 3(b) the center of the spheres represent the experimental points for each liquid. Similar adjustments were made for the other two samples.

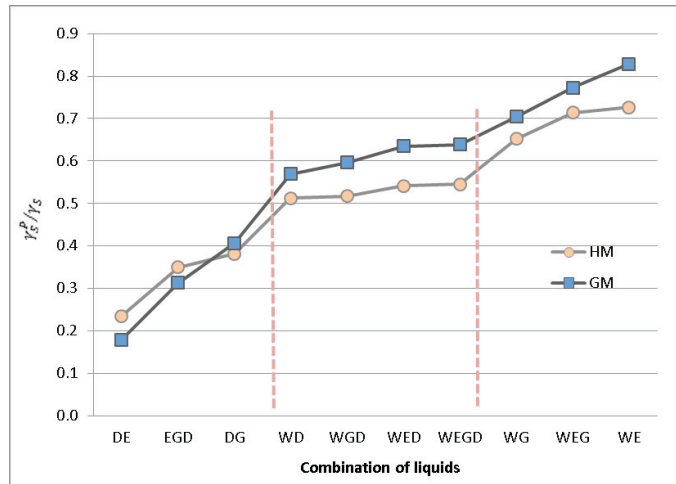


Fig. 4. Ratio of the polar component  $\gamma_S^p$  over the total  $\gamma_S$  for all the di, tri and four liquids combinations obtained by the HM and GM methods.  
Ref: W: Water – E: Ethylene glycol – G: Glycerol – D: Dimethyl sulfoxide

Obtaining the values reported in Table 3 for each component  $\gamma_S^d$  and  $\gamma_S^p$ , the  $\gamma_S$  and the ratio  $\gamma_S^p / \gamma_S$ ; it is noted as in the case of the results obtained with the GM method, the high dispersion in the values of the contribution of each component calculated with the different combinations of liquids, regardless of the number of liquids employed and the fact that the  $\gamma_S$  give similar values. The values of the ratio shown in the last column for  $\gamma_S^p / \gamma_S$  show that the more stable and reproducible ratios correspond to those values calculated using water and dimethyl sulfoxide, as in the case of the GM method. This is illustrated in Figure 5(a) in which again the combinations which include the following two liquids, WD, WE, DG, DE and GE give similar results and the smallest error or dispersion in the results. In the case of the calculations made using only two liquids the results may be inconsistent with the physical problem and without any physical meaning. This is the result of the mathematics since in a system of non-linear equations, more than one solution is possible, for instance in the case of the calculations using glycerol and dimethyl sulfoxide there are two set of results:  $\gamma_S^d=211.85$ ,  $\gamma_S^p=-4.30$  and  $\gamma_S^d=28.39$ ,  $\gamma_S^p=16.86$ . In this case it is obvious that the second set has no physical meaning, and the first set is chosen, however, in other cases the choice may not be so clear and the duality must be solved properly.

Table 4. Surface free energy ( $\text{mJ/m}^2$ ) obtained using LW/AB method

Liquids	$\sqrt{\gamma_S^{LW}}$	$\sqrt{\gamma_S^-}$	$\sqrt{\gamma_S^+}$	$\gamma_S^{LW}$	$\gamma_S^{AB}$	$\gamma_S$
WEGD	5.2	5.6	1.4	26.9	15.7	42.7
WEG	-11.6	13.7	8.8	134.6	240.4	375.0
WED	6.3	0.3	5.7	39.1	3.4	42.5
EGD	8.7	-3.3	14.2	74.8	-94.0	-19.1
WGD	4.5	2.2	5.4	20.5	23.4	43.9



3.2.4. Lifshitz-van der Waals/Acid-Base Method (LW/AB)

With the contact angles measured for the four liquids a linear fitting by the least square method was performed for each of the four combinations of three liquids, of Equation 13. In addition the four CA measured were fitted to the same equation. The results of the fitting process are shown in Table 4 for each of the components;  $\sqrt{\gamma_S^{LW}}$ ,  $\sqrt{\gamma_S^-}$  and  $\sqrt{\gamma_S^+}$ , and  $\gamma_S^{LW}$  and  $\gamma_S^{AB}$  and the addition gives  $\gamma_S$  in the last column. In Table 4 the large variation in the results for the components is observed, even the negative with no physical meaning like in the case of the combinations WEG and EGD. In the case of the combinations EGD the calculated  $\gamma_S$  results negative (-19.1 mJ/m<sup>2</sup>) and in the case of the WEG combination a  $\gamma_S$  value of 375.0 mJ/m<sup>2</sup>. These anomalous results cannot be explained. On the contrary the SFE calculated using the other three combinations WEGD, WED and WGD are similar; 42.7mJ/m<sup>2</sup>, 42.5 mJ/m<sup>2</sup> and 43.9 mJ/m<sup>2</sup> respectively.

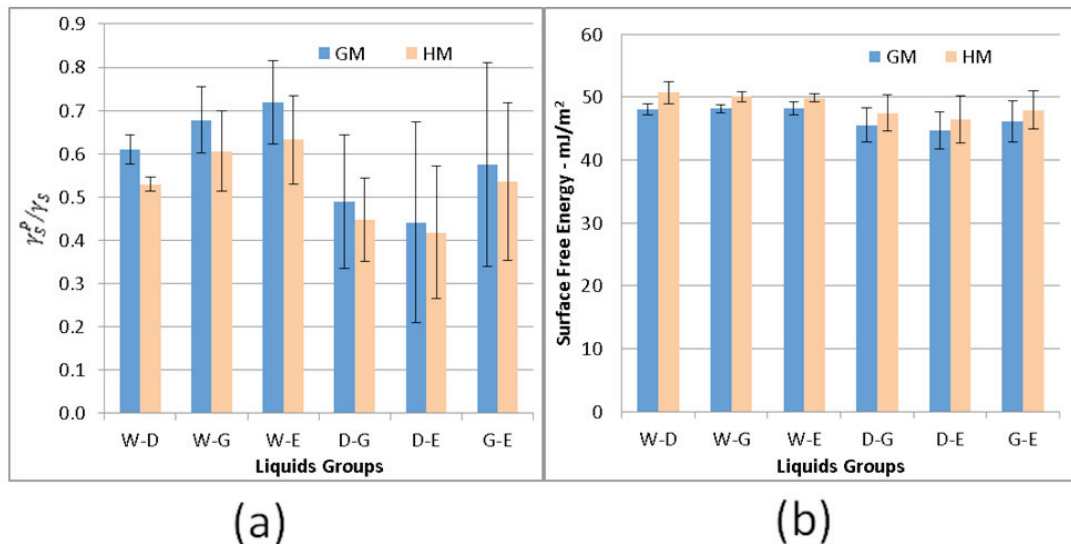


Fig. 5. Polar component to the total SFE ratio (a) and total SFE (b) as a function of the 6 possible combinations of the liquids in all possible combination of the four liquids.

Ref. W: Water – E: Ethylene glycol – G: Glycerol – D: Dimethyl sulfoxide.

In the three combinations, water and dimethyl sulfoxide are always used. It is observed that despite the fact that the final values are similar, the SFE components change substantially among the three combinations of liquids. Therefore, for comparison purposes only the last three results for WEGD, WED and WGD are selected and included in Table 3.

Table 5. Surface free energy (mJ/m<sup>2</sup>) of TiO<sub>2</sub>, calculated with the Equation of State of different liquids.

Liquids	$\gamma_s$
Water (W)	52.7 ± 0.6
Glycerol (G)	47.0 ± 0.3
Ethylene glycol (E)	42.0 ± 0.1
Dimethyl sulfoxide (D)	40.1 ± 0.3
Mean	45.4 ± 5.6

3.2.5. The Equation of State Method (ES)

Using Equation 15 and the measured contact angles for each liquid in the three samples, the SFE was calculated and listed in Table 5. It is observed that the calculated values of  $\gamma_s$  span from 40.1 mJ/m<sup>2</sup> for ethylene glycol to 52.7 mJ/m<sup>2</sup> for water. The average value is 45.4 ± 5.6 mJ/m<sup>2</sup>.

It is noted that the present method permits the calculation of the  $\gamma_S$  and not the polar and dispersive components, which may be important in the analysis of its behavior when it is in contact with other substances. Moreover, it is not clear in the method if  $\beta_1$  is a universal constant or depends on each material.

#### 4. Conclusions

The analysis of the results of the surface free energy of the Ti6Al4V determined by five different methods: the Zisman method, the geometric mean method, the harmonic mean method, the Lifshitz-van der Waals / Acid-Base method and the equation of state method, permit to conclude the following:

- The results are very dependent of the method as well as the liquids employed.
- The value of SFE ( $\gamma_S$ ) obtained by the Zisman method is systematically 20% lower than the values obtained by the other four methods.
- Properly choosing the liquids, the other four methods; the geometric mean method, the harmonic mean method, the Lifshitz-van der Waals / Acid-Base method and the equation of state method, results in calculated values of  $\gamma_S$  which are similar, between 42 and 50 mJ/m<sup>2</sup>.
- The geometric mean and harmonic mean methods produce similar values of dispersive  $\gamma_S^d$  and polar  $\gamma_S^p$  component for the same combinations of liquids.
- The calculated values of dispersive  $\gamma_S^d$  and polar  $\gamma_S^p$  components vary substantially, depending on the liquids used.
- The total SFE ( $\gamma_S$ ) as well as the component of SFE ( $\gamma_S^d$  and  $\gamma_S^p$ ) of the Ti6Al4V obtained by the geometric mean method, the harmonic mean method and the Lifshitz-van der Waals / Acid-Base method are very similar ( $\gamma_S^d = 21.5 \pm 2.7$  mJ/m<sup>2</sup>,  $\gamma_S^p = 26.1 \pm 2.7$  mJ/m<sup>2</sup> and  $\gamma_S = 47.6 \pm 3.5$  mJ/m<sup>2</sup>) with a total maximum dispersion of 12 % among the results when proper combination of liquids are used, as in the present case using water, glycerol and dimethyl sulfoxide.
- The equation of the geometric mean method when linearized, simplifies the calculation process without losing precision.

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