

## The influence of oleate adsorption at the fluorite/water interface on fluorite surface free energy

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Received 8 February 1993; accepted for publication 19 June 1993

Contact-angle measurements for water, glycerol, formamide, di-iodomethane and bromoform on fluorite plates covered with a film of oleate are made. Using the contact-angle values, the Lifshitz–van der Waals component and the electron–acceptor parameter of the surface free energy of the fluorite/oleate film are calculated. On the basis of the contact-angle measurements and the calculations done, it is found that at low equilibrium oleate concentration the surface free energy of the fluorite/oleate film comes close to the value for paraffin, however at high oleate concentration, the surface of the fluorite/oleate film can interact with the adherent phase not only by Lifshitz–van der Waals forces but also by acid–base forces. It results from a hydration process which takes place at the highest sodium oleate concentrations. It is stated that the considerable decrease of the fluorite/oleate–film–water interfacial free energy at oleate species concentration higher than 87.1 mg/dm<sup>3</sup> can also result from electrostatic interactions across the interface.

### 1. Introduction

The adsorption of surfactants is important in a great number of technological areas including, among others, froth flotation of minerals [1]. Froth flotation of fluorite (CaF<sub>2</sub>) frequently involves the use of fatty acids as surfactants to render the mineral particles hydrophobic and floatable. One acid commonly used for this purpose is oleic acid. In the alkaline environments of most of the fluorite flotation circuits, the oleate species are predominantly in the ionized form [2].

The oleate ions adsorbed at the fluorite/water interface strongly change the properties of the fluorite surface [3,4], which are related to its surface free energy. Then, the determination of the surface free energy of fluorite covered with an adsorbed film of oleate can be useful for a

better understanding of the attachment of gas bubbles to the fluorite particles in the flotation process.

Since it is not possible to measure directly the surface free energy of a solid phase, there are, at present, many indirect methods to determine it. Among others, the methods based on the measurement of the contact angle for proper systems are the most popular. These methods involve the use of two basic approaches, the first one is based on the assumption that the surface free energy of a solid or a liquid can be divided into components owing to different kinds of intermolecular interactions. In the second approach it is assumed that the surface free energy cannot be divided into components [5–13].

In the first group, the approach proposed recently by van Oss et al. [10–13] is often used to determine the components of the surface free energy of solids. This approximation seems to be very convincing. In general, this approach assumes that any surface can exhibit two types of interactions: one apolar, from Lifshitz–van der

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Waals interactions, and one polar, due to Lewis acid–base, i.e., electron–acceptor and electron–donor interactions.

The main purpose of our study is the determination of the Lifshitz–van der Waals and the acid–base components of the surface free energy of fluorite covered with an adsorbed film of oleate on the basis of the contact-angle measurements for properly chosen systems.

## 2. Experimental

### 2.1. Materials

The fluorite used in this study came from Cerro Muriano (Córdoba, Spain) (purity, more than 99%). The crystals, translucent and with a greenish tint, were selected and polished with abrasive paper of various grades, to obtain plates of good quality without any irregularity. Then, the plates were washed several times in doubly distilled and de-ionized water, placed in an ultrasonic bath for 15 min, and finally dried at 50°C for 30 min.

Sodium oleate was a Fluka product (purity > 99%) and was stored in a refrigerator at –18°C. Water used in the experiments was doubly distilled and de-ionized. Anhydrous glycerol (purity > 99.5%), formamide (purity > 99%) and di-iodomethane (purity > 99%) were from Merck, and bromoform (purity > 99%) was from Aldrich.

### 2.2. Methods

Sodium oleate was dissolved in doubly distilled and de-ionized water. The pH of the solution was adjusted to  $9.5 \pm 0.1$  using solutions of HCl and NaOH.

The fluorite plates were immersed into solutions of sodium oleate with concentrations ranging between 2.85 and 185.00 mg/dm<sup>3</sup>. Plates were kept in the solution for 24 h. This time was sufficient to ensure the maximum oleate adsorption onto the fluorite surface at each concentration. Then plates were dried at 50°C for 30 min.

All measurements of the advancing contact angle were carried out at  $20 \pm 1^\circ\text{C}$  by the sessile-

drop method [14] using a camera–computer system described elsewhere [15]. Drops were dispensed with a Hamilton microsyringe and the measurements were made immediately after the drop was settled onto the fluorite surface.

For a given system the contact-angle measurements were repeated several times, with an accuracy within 2°.

## 3. Results

The contact angles of water ( $\theta_W$ ), glycerol ( $\theta_G$ ), formamide ( $\theta_F$ ), di-iodomethane ( $\theta_D$ ) and bromoform ( $\theta_B$ ) on the fluorite surface, on which sodium oleate was previously adsorbed, are shown in table 1 as a function of the sodium oleate concentration in the equilibrium solution. From this table it appears that the values obtained with di-iodomethane and bromoform hardly change but slightly increase with the sodium oleate concentration. However, comparing these  $\theta_D$  and  $\theta_B$  values to those measured earlier [16] in the system “pure” fluorite (fluorite not covered with sodium oleate) – di-iodomethane drop – air and “pure” fluorite – bromoform drop – air, important differences are observed between them. For both liquids the  $\theta_D$  and  $\theta_B$  values increase more than 20° after the fluorite surface was covered with the adsorbed film of oleate.

Table 1  
Measured values of contact angle for water ( $\theta_W$ ), glycerol ( $\theta_G$ ), formamide ( $\theta_F$ ), di-iodomethane ( $\theta_D$ ) and bromoform ( $\theta_B$ ) on fluorite surface covered with adsorbed oleate film

Concentration (mg/dm <sup>3</sup> )	Contact angle (deg)				
	$\theta_W$	$\theta_G$	$\theta_F$	$\theta_D$	$\theta_B$
0.00 <sup>a)</sup>	82.2	72.6	65.7	44.1	18.0
2.85	110.7	99.3	93.1	66.1	56.3
5.70	110.4	97.4	93.0	66.3	56.4
14.00	109.6	97.0	92.7	67.4	57.6
30.00	108.9	96.9	93.0	67.7	57.8
59.20	108.1	96.0	92.5	68.8	58.1
87.10	106.6	94.3	90.7	69.4	58.4
128.50	94.1	86.0	83.5	71.2	59.0
185.00	80.0	82.7	80.2	71.8	59.6

<sup>a)</sup> From ref. [16].

The contact-angle values for water, glycerol and formamide decrease when the sodium oleate concentration increases from 2.85 to 185 mg/dm<sup>3</sup>. However, the variation of  $\theta_W$ ,  $\theta_G$  and  $\theta_F$  has two different behaviors in that range of concentration. In the first interval, corresponding to concentrations up to 87.1 mg/dm<sup>3</sup>, the contact angles are considerable but decrease a few degrees when the concentration increases. In the second interval, which includes concentrations between 87.1 and 185 mg/dm<sup>3</sup>, a great decrease of the  $\theta_W$ ,  $\theta_G$  and  $\theta_F$  values is observed. However, the minimum values of the contact angle for glycerol and formamide are 10° higher than those contact angles obtained for the system “pure” fluorite – glycerol drop – air and “pure” fluorite – formamide drop – air [16]. For water, the value of the contact angle corresponding to the highest concentration (185 mg/dm<sup>3</sup>) is nearly the same as for “pure” fluorite.

For the three polar liquids studied, the adsorption of oleate ions on the fluorite surface from the solutions with low sodium oleate concentration changes the contact-angle values more than 25° in relation to “pure” fluorite.

#### 4. Calculations

On the basis of the data presented in table 1, the components of the surface free energy of fluorite/oleate film can be determined by using Young’s equation:

$$\gamma_S - \gamma_{SL} - \Pi e_L = \gamma_L \cos \theta_L, \quad (1)$$

where  $\gamma_S$  is the surface free energy of the solid,  $\gamma_{SL}$  is the interfacial solid/liquid free energy,  $\gamma_L$  is the surface free energy of the liquid,  $\theta_L$  is the contact angle and  $\Pi e_L$  is the film pressure of the liquid, which can be assumed to be equal to zero for low-energetic solids [5]. However, one of the problems arising when Young’s equation is used for this purpose is the formulation of the interfacial solid/liquid free energy ( $\gamma_{SL}$ ) in terms of the surface free energy of the solid ( $\gamma_S$ ) and of the liquid ( $\gamma_L$ ).

In the literature [5–13,16–21] there are many approaches dealing with the solid/liquid and liq-

uid/liquid interfacial free energy. Among them an approach to the solution of this problem has been recently suggested by van Oss et al. [10–13]. Using their approach in Young’s equation for  $\Pi e_L = 0$ , leads to:

$$\gamma_L (\cos \theta_L + 1) = 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} + 2(\gamma_S^+ \gamma_L^-)^{1/2} + 2(\gamma_S^- \gamma_L^+)^{1/2}, \quad (2)$$

where the  $\gamma^{LW}$  is the component of the solid or liquid surface free energy which results from Lifshitz–van der Waals interactions and  $\gamma^+$  and  $\gamma^-$  are electron–acceptor (Lewis acid) and electron–donor (Lewis base) parts of the acid–base component,  $\gamma^{AB}$ , of the solid or liquid surface free energy. Subscripts S and L refer to solid and liquid, respectively.

Component  $\gamma^{AB}$  of the free energy results from hydrogen-bond interactions and can be expressed [10–13]:

$$\gamma^{AB} = 2(\gamma^+ \gamma^-)^{1/2}. \quad (3)$$

If the acid–base interactions at the solid/liquid interface are absent, eq. (2) can be rewritten in the form:

$$\gamma_L (\cos \theta_L + 1) = 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2}. \quad (4)$$

Introducing into eq. (4) the values of  $\gamma_L^{LW}$  (table 2) taken from the literature [10,19,21] and the measured values of the contact angle for water, glycerol, formamide, di-iodomethane and bromoform, the  $\gamma_S^{LW}$  values were calculated and are presented in table 3.

As can be seen from table 3, the  $\gamma_S^{LW(D)}$  and  $\gamma_S^{LW(B)}$  values decrease when the sodium oleate concentration does. For the  $\gamma_S^{LW(W)}$ ,  $\gamma_S^{LW(G)}$  and

Table 2  
Values of Lifshitz–van der Waals ( $\gamma_S^{LW}$ ), electron–acceptor ( $\gamma_S^+$ ) and electron–donor ( $\gamma_S^-$ ) components of liquid surface tension taken from the literature [10,19,21], in mN/m

Liquid	$\gamma_L^{LW}$	$\gamma_L^+$	$\gamma_L^-$	$\gamma_L$
Water	21.80	25.5	25.5	72.8
Glycerol	33.11	10.74	21.23	63.3
Formamide	31.72	9.95	17.83	58.4
Di-iodomethane	50.8	0.72	0.0	50.8
Bromoform	41.5	1.72	0.0	41.5

$\gamma_S^{LW}(F)$  values the reversed dependence is evident. However, there are only slight differences among the  $\gamma_S^{LW}$  values in the range of sodium oleate concentration from 2.85 to 59.20 mg/dm<sup>3</sup>.

It is known that the surface free energy of di-iodomethane and bromoform results from Lifshitz–van der Waals intermolecular interactions, however, these liquids can also interact with the contacting phase by a weak electron–acceptor force [10,19,21]. Since for a given sodium oleate concentration, the values of  $\gamma_S^{LW}(D)$  and  $\gamma_S^{LW}(B)$  are the same (within the contact-angle measurement error) and the electron–acceptor part of the acid–base component for bromoform is more than two times higher than for di-iodomethane [19,21] eq. (4) is thus fulfilled in the total range of sodium oleate concentration only for di-iodomethane and bromoform ( $\gamma_L^- = 0$  and  $\gamma_S^- = 0$ ).

Therefore, introducing into eq. (2) the  $\gamma_S^{LW}(D)$  values as the Lifshitz–van der Waals components of fluorite/oleate film surface free energy and components of liquid surface tension for water, glycerol and formamide taken from the literature [21] (table 2) and their contact angles (table 1) the  $\gamma_S^+$  values were calculated and are presented in table 4.

From table 4 it is seen that in the range of sodium oleate concentration from 2.85 to 59.2

Table 3

Values of Lifshitz–van der Waals ( $\gamma_S^{LW}$ ) components of fluorite/oleate film surface calculated from eq. (4) using the contact angle for water,  $\gamma_S^{LW}(W)$ , glycerol,  $\gamma_S^{LW}(G)$ , formamide,  $\gamma_S^{LW}(F)$ , di-iodomethane,  $\gamma_S^{LW}(D)$  and bromoform,  $\gamma_S^{LW}(B)$ , in mJ/m<sup>2</sup>

Concentration (mg/dm <sup>3</sup> )	$\gamma_S^{LW}(W)$	$\gamma_S^{LW}(G)$	$\gamma_S^{LW}(F)$	$\gamma_S^{LW}(D)$	$\gamma_S^{LW}(B)$
2.85	25.40	21.27	24.05	25.08	25.08
5.70	25.79	22.96	24.14	24.96	25.04
14.00	26.84	23.33	24.41	24.34	24.47
30.00	27.78	23.42	24.14	24.17	24.38
59.20	28.88	24.26	24.59	23.55	24.24
87.10	31.74	25.89	26.23	23.21	24.10
128.50	52.40	34.62	33.31	22.20	23.81
185.00	83.72	38.43	36.81	21.87	23.53

The values of surface free energy for “pure” fluorite are:  $\gamma_S^{LW} = 34.03$ ;  $\gamma_S^+ = 0.13$ ;  $\gamma_S^- = 5.91$  (from ref. [16]).

Table 4

Values of the electron–acceptor,  $\gamma_S^+$ , part of the acid–base component,  $\gamma_S^{AB}$ , calculated from eq. (2) using the contact angle for water,  $\gamma_S^+(W)$ , glycerol,  $\gamma_S^+(G)$  and formamide,  $\gamma_S^+(F)$ , in mJ/m<sup>2</sup>

Concentration (mg/dm <sup>3</sup> )	$\gamma_S^+(W)$	$\gamma_S^+(G)$	$\gamma_S^+(F)$
2.85	0.001	0.245 <sup>a)</sup>	0.019 <sup>a)</sup>
5.70	0.006	0.065 <sup>a)</sup>	0.012 <sup>a)</sup>
14.00	0.052	0.017 <sup>a)</sup>	0.000
30.00	0.108	0.009 <sup>a)</sup>	0.000
59.20	0.233	0.008	0.020
87.10	0.482	0.114	0.164
128.50	5.459	2.144	1.998
185.00	17.107	3.616	3.440

<sup>a)</sup> Square root is negative.

mg/dm<sup>3</sup> the  $\gamma_S^+$  values are negligible but increase when the concentration rises from 87.10 to 185 mg/dm<sup>3</sup>.

It is interesting to note that in the range of sodium oleate concentration from 87.10 to 185 mg/dm<sup>3</sup> the  $\gamma_S^+(G)$  and  $\gamma_S^+(F)$  values are the same and both lower than the  $\gamma_S^+(W)$  ones.

Comparing the  $\gamma_S^{LW}$  and  $\gamma_S^+$  values for fluorite/oleate film to those for “pure” fluorite [16] it is seen that the  $\gamma_S^{LW}$  component for “pure” fluorite is higher than for fluorite covered with an oleate film, however, the  $\gamma_S^+$  values at high concentration are higher than for “pure” fluorite. It should be emphasized that for “pure” fluorite the  $\gamma_S^-$  value is higher than zero.

It is worth emphasizing that the  $\gamma_S^{LW}$  values for fluorite/oleate film corresponding to a sodium oleate concentration from 2.85 to 59.20 mg/dm<sup>3</sup> are close to the surface free energy of paraffin [20].

## 5. Discussion

Fluorite is a semisoluble mineral and the surface free energy for “dry” fluorite results from Lifshitz–van der Waals intermolecular interactions only [16]. However, after the contact of fluorite with water its surface free energy results, apart from Lifshitz–van der Waals, also from

acid–base intermolecular interactions. The magnitude of the acid–base component depends on the time of contact of fluorite with water, and on the pH.

It is recognized in the fluorite/oleate system that important collector reactions including chemisorption, surface precipitation and aqueous-phase precipitation [3,4] can take place.

The isotherm of oleate adsorption on fluorite surface indicates three distinct regions.

At low equilibrium oleate concentration (up to 8.13 mg/dm<sup>3</sup>) there is a plateau region with a little variation in the adsorption density [3]. In this region the adsorbed species are chemisorbed at the fluorite/water interface and the hydrocarbon chains are oriented parallel to the fluorite surface plane if the oleate adsorption density is not greater than 0.5 mg/m<sup>2</sup> [4,22].

The chemisorbed oleate molecules are mono-coordinated to the fluorite surface through the oxygen atoms in the polar head group. The initially adsorbed oleate species have few nearest neighbors and consequently the alkyl chains are highly mobile with a significant number of gauche bonds [4].

As a result of chemisorption the fluorite surface free energy decreases (table 3). The Lifshitz–van der Waals component drops from about 34 to 25 mJ/m<sup>2</sup>. This last value is nearly the same as for the surface free energy of paraffin [20]. The electron–acceptor ( $\gamma_S^+$ ) and the electron–donor ( $\gamma_S^-$ ) parts of the acid–base component for fluorite after adsorption decrease almost to zero (tables 3 and 4) [16]. Therefore, at the region of low oleate concentration, there are good conditions to make a fluorite surface with quite hydrophobic properties. The contact angle of water on the fluorite/oleate film surface is the same as on paraffin surface (table 1) [20]. This fact is very important in the flotation process of fluorite.

At higher equilibrium oleate concentration (> 8.13 mg/dm<sup>3</sup>), the adsorption density increases with the equilibrium concentration up to a maximum value (27 mg/dm<sup>3</sup>) [3], associated to a multilayer adsorption, after which it drops. According to Keller et al. [3] around the oleate concentrations bringing about the maximum adsorption

density, the surface precipitation of the calcium oleate salt takes place.

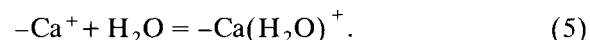
The increase of chemisorbed oleate species on fluorite surface leads to an interaction of alkyl chains through van der Waals forces and the number of gauche bonds have been reduced stabilizing the alkyl chains in a more rigid trans state.

Probably, the slight decrease of  $\gamma_S^{LW}$  values observed in the range of sodium oleate concentration from 2.85 to 30.0 mg/dm<sup>3</sup> (table 3) comes as result of the changes from gauche to trans state.

In the region of precipitation, the  $\gamma_S^{LW}$  components for the fluorite/oleate film surface free energy decrease until the value for water and those for the electron–acceptor part of the acid–base interactions increase, but  $\gamma_S^-$  is equal to zero. It means that, together with the precipitation process, the fluorite/oleate film surface is hydrated and the water molecules are strongly oriented since only electron–acceptor interactions were detected (table 4).

However, the  $\gamma_S^+$  values determined from the contact angle for glycerol and formamide are generally lower than those from the contact angle for water (table 4) which may suggest that not only acid–base interactions resulting from hydrogen bonds take place at the fluorite/oleate film–water interface but also interactions resulting from electrostatic forces.

Probably, on the fluorite/oleate film surface some  $-Ca^+$  defects exist and water molecules can react with this ion according to:



These defects lead not only to the presence of acid–base interactions where H<sub>2</sub>O molecules are the origin of the electron–acceptor part (oxygen is directed to the Ca<sup>+</sup> ion) of these interactions but probably also to a positively charged fluorite/oleate film surface.

The presence of acid–base and electrostatic interactions decreases the interfacial fluorite/oleate film–water free energy and consequently decreases the contact angle.

From our calculations it results that in the range of sodium oleate concentration from 2.85

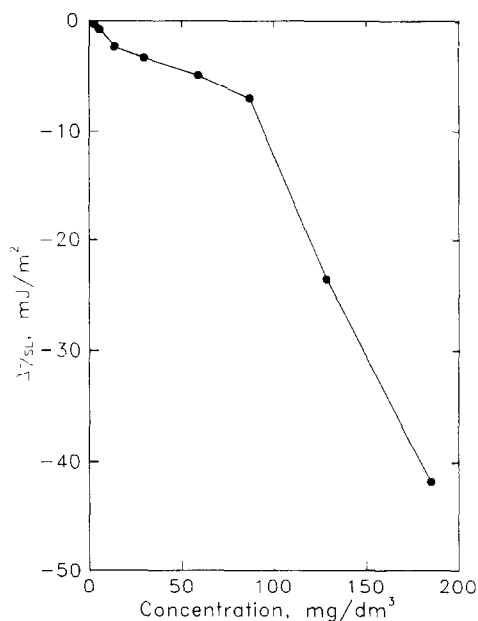


Fig. 1. Dependence between  $\Delta\gamma_{SL}$  and concentration of sodium oleate.

to 185 mg/dm<sup>3</sup> the electron-donor part of the acid-base component of the fluorite/oleate film surface free energy is equal to zero. Thus according to eq. (3) the term  $\gamma_S^{AB} = 0$  and the total surface free energy of fluorite covered with oleate film is equal to  $\gamma_S^{LW}$ .

According to the Lippmann equation [23,24] the electrified solid/liquid interface free energy appears to go through a maximum at the pzc. Therefore, the fluorite/oleate film-water interface free energy should assume the maximum value calculated from the following equation:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^{LW}\gamma_L^{LW})^{1/2}. \quad (6)$$

However, the real fluorite/oleate film-water interfacial free energy can be determined from Young's equation (1):

$$\gamma_{SL} = \gamma_S - \gamma_L \cos \theta_L. \quad (7)$$

Taking into account  $\gamma_S = \gamma_S^{LW}(D)$  (table 3) the differences in the  $\Delta\gamma_{SL}$  values were calculated from eqs. (6) and (7), respectively, and are shown in fig. 1.

From this figure it is clearly seen that the more significant decrease of the fluorite/oleate film-

water interfacial free energy appears at an equilibrium oleate concentration higher than 87.1 mg/dm<sup>3</sup>. For such concentration a high surface precipitation takes place [3,4].

The decrease of the  $\gamma_{SL}$  value can be related with the positively charged fluorite/oleate film surface at the fluorite/oleate film-water interface and therefore we observe higher values of  $\gamma_S^+$  determined from the contact angle for water than for glycerol and formamide (table 4). Probably, some part of the  $\gamma_S^+(W)$  value includes the electrostatic contribution to the interactions at the fluorite/oleate film-water interface. It is not very probable that electrostatic interactions influence the contact angle of such organic liquids as glycerol and formamide. However, we have not sufficient experimental proof to conclude with certitude that the differences in the  $\gamma_S^+$  values obtained from the contact angle for water and for polar organic liquids come from electrostatic interactions.

On the basis the above-mentioned results it can be stated that from the point of view of the flotation process of fluorite the best condition for the attachment of particles to air bubbles exists at low sodium oleate concentration where only the chemisorption of oleate occurs, and the fluorite/oleate film surface interacts with the adherent medium only by Lifshitz-van der Waals forces.

### Acknowledgement

Financial support for this work by DGICYT under project No. PB89-0519 is gratefully acknowledged.

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