Wettability and surface tension of fluorite

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Abstract

Measurements of the contact angle for water, glycerol, formamide, diiodomethane and bromoform on a fluorite surface with different initial treatments were carried out. Using the measured values of contact angle, the Lifshitz–van der Waals and the acid–base components of the surface tension of fluorite were calculated. The electron-acceptor and electron-donor parts of the acid–base component were also determined. From these results it appears that "dry" fluorite is hydrophobic and that only Lifshitz–van der Waals intermolecular interactions are the origin of its surface tension. Under the influence of water, HF and Ca(OH)$_2$ aqueous solutions, the fluorite surface exhibits hydrophilic behaviour, and its tension, apart from Lifshitz–van der Waals intermolecular interactions, results from acid–base interactions due to the hydration process taking place in the treatment.

Introduction

The most important fluoride of the alkaline earths is calcium fluoride, known in its mineral form as fluorite. It is the only large-scale mineral source of fluorine. Therefore, from a practical point of view, the recovery of fluorite is important. Flotation, among others, is a technique widely used for the concentration or purification of mineral particles, resulting from the attachment of gas bubbles to the particles while they are suspended in aqueous solution. This process is governed by the interfacial interactions between mineral and solution and between mineral and gas, but can be changed by addition of various chemicals. One of the possible ways of obtaining information on these interactions is to study the surface tension components of the mineral.

Among many attempts to describe the solid–liquid and solid–gas interfacial interactions [1–10], the recent proposals by van Oss and co-workers [7–10] seem to be adequate, in particular for minerals such as fluorite, for which hydration and adsorption of water molecules cannot be excluded.

In general, any surface can exhibit two types of interaction; one is apolar (by Lifshitz–van der Waals forces) and the other is polar (by Lewis acid–base interactions), giving rise, respectively, to the Lifshitz–van der Waals, the electron-acceptor and the electron-donor components of its surface tension.

The main purpose of this work was the determination of these components for the fluorite surface and their dependence on the drying procedure and the method of preparation of fluorite plates, on the basis of contact angle measurements for appropriately chosen systems.

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Experimental

The advancing contact angles were measured at $20 \pm 1°C$ by the sessile drop method [11] using the goniometer–camera–computer system described elsewhere [12].

The mineralogical species of fluorite came from Cordoba, Spain. The samples of fluorite were cut into plates and polished with abrasive paper of various grades. The plates were washed several times in doubly distilled and deionized water and placed in an ultrasonic bath for 15 min. The plates were then prepared by three different methods.

In the first method the sample was dried at 50°C for 30 min (fluorite Ia) or at 110°C for 2 h (fluorite Ib). After cooling to room temperature, the plate was placed in the measuring chamber and immediately a drop of a given liquid of about 2 mm³ was settled by a Hamilton microsyringe and the contact angle was measured with the aid of a computer.

In the second method of preparation, the plates were immersed in an aqueous solution of HF (0.1 M) for 10 min. They were then washed several times in doubly distilled and deionized water and dried at 50°C for 30 min (fluorite IIa) or at 110°C for 2 h (fluorite IIb). After cooling to room temperature, the contact angle was measured by the previous procedure.

The third method of preparation of the fluorite plates was similar to the second, except that they were immersed in an aqueous solution of $Ca(OH)_2$ (0.1 M) for 10 min instead of in an HF solution. These plates were called fluorite IIIa (sample dried at 50°C for 30 min) or fluorite IIIb (sample dried at 110°C for 2 h).

For a given system, the contact angle measurements were repeated several times. The precision of the contact angle measurements was within $\pm 2°$.

The following liquids were used for measurements: water, doubly distilled and deionized; anhydrous glycerol (Fluka, purity > 99.5%); formamide (Fluka, purity > 99%), diiodomethane (Fluka, purity > 98%); bromoform (Aldrich, purity > 99%).

Each liquid is henceforth identified by its initial letter.

Results

The average values of the contact angle for water (θ_W), glycerol (θ_G), formamide (θ_F), diiodomethane (θ_D) and bromoform (θ_B) on a fluorite surface are shown in Table 1. From this table it is seen that in the case of diiodomethane (an apolar liquid) only slight changes in contact angle are observed for the fluorite plates studied. However, for bromoform (also an apolar liquid) the most important difference between the values of the contact angle comes from the drying procedure.

For the polar liquids water, glycerol and formamide the contact angle strongly depends on the method of preparation of the fluorite plates before measurements. The greatest change in contact angle occurs for fluorite II. This means that after treatment of the fluorite plate by the aqueous HF solution and drying at 50°C, water and formamide spread completely over the fluorite IIa surface; the value of the contact angle for glycerol is the lowest among all the systems studied (16.7°). However, after drying the fluorite plate at 110°C (fluorite IIb) the values of θ_W, θ_G and θ_F increase to 98.6°, 79.7° and 65.3° respectively.

With the exception of fluorite IIa, the highest contact angle is obtained for water and the lowest for bromoform. In the case of fluorite IIa the highest value is observed for diiodomethane.

Table 1
Measured values of contact angle for water (θ_W), glycerol (θ_G), formamide (θ_F), diiodomethane (θ_D) and bromoform (θ_B) on a fluorite surface

Fluorite sample	θ_W	θ_G	θ_F	θ_D	θ_B
Ia	82.2	72.6	65.7	44.1	18.0
Ib	100.6	81.8	69.9	46.8	27.1
IIa	0.0	16.7	0.0	45.0	10.0
IIb	98.6	79.7	65.3	46.9	26.6
IIIa	53.1	53.0	49.5	43.1	15.0
IIIb	88.0	72.0	61.3	47.9	26.4

It is interesting to note that after treatment of the fluorite plate by $Ca(OH)_2$ solution and drying at $50°C$, the contact angles for water, glycerol and formamide differ only slightly, and they are no more than $10°$ higher than the value of the contact angle for diiodomethane.

As found for polar liquids, the contact angles of apolar liquids on fluorites Ia, IIa and IIIa are lower than on fluorites Ib, IIb and IIIb respectively. This means that after drying the fluorite plates at $110°C$ an increase is observed in the θ_D and θ_B values relative to the values obtained for the plates dried at $50°C$. Further, for all the samples studied the values of contact angles observed for diiodomethane are higher than those for bromoform.

Calculations

From contact angle measurements it is possible to calculate the components of the surface tension of fluorite using Young's equation:

$$\gamma_S - \gamma_{SL} - \Pi e_L = \gamma_L \cos \theta_L \tag{1}$$

where γ_S is the solid surface tension, γ_{SL} is the interfacial solid–liquid tension, γ_L is the liquid surface tension, θ_L is the contact angle and Πe_L is the film pressure of the liquid, which is equal to zero for low energy solids [1].

According to van Oss and co-workers [7–10], for liquids and solids the surface tension can be divided into two components:

$$\gamma = \gamma^{LW} + \gamma^{AB} \tag{2}$$

where γ^{LW} is an apolar component resulting from Lifshitz–van der Waals intermolecular interactions (London, Debye and Keesom forces) and γ^{AB} is the component resulting from electron-acceptor (Lewis acid) and electron-donor (Lewis base) intermolecular interactions. Van Oss and co-workers stated that dipole–dipole interactions such as the Keesom forces make, at most, a small contribution to the surface tension because of their mutual saturation.

For the γ^{AB} component of the surface tension

the following equation holds [7–10]:

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

where γ^+ and γ^- are the contributions to γ^{AB} from electron-acceptor and electron-donor interactions respectively.

For a solid–liquid system its interfacial tension γ_{SL} can be expressed [7–10] in the form

$$\gamma_{SL} = [(\gamma_S^{LW})^{1/2} - (\gamma_L^{LW})^{1/2}]^2 \\ + 2[(\gamma_S^+)^{1/2} - (\gamma_L^+)^{1/2}][(\gamma_S^-)^{1/2} - (\gamma_L^-)^{1/2}] \tag{4}$$

where subscripts S and L refer to solid and liquid phases respectively.

Introducing Eq. (4) into Eq. (1), for $\Pi e_L = 0$, gives

$$\gamma_L(\cos \theta_L + 1) = 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} + 2(\gamma_S^+ \gamma_L^-)^{1/2} \\ + 2(\gamma_S^- \gamma_L^+)^{1/2} \tag{5}$$

With the aid of Eq. (5) it is possible to determine the γ_S^{LW}, γ_S^+ and γ_S^- components of the surface tension of a solid on the basis of contact angle measurements for three different liquids on the same solid surface.

For fluorite, five liquids were used for contact angle measurements. Thus there are ten different possibilities for calculating the γ_S^{LW}, γ_S^+ and γ_S^- values, which are denoted by three letters corresponding to the first letter of each combination of three liquids employed.

Nevertheless, according to our previous calculations [13] and the studies of van Oss et al. [8,9], the values of γ_S^{LW}, γ_S^+ and γ_S^- obtained from the systems of three liquids GDW, FDW, GBW and FBW are encumbered with the lowest errors. Therefore, introducing into Eq. (5) the values of γ_L^{LW}, γ_L^+ and γ_L^- for water, glycerol, formamide, diiodomethane and bromoform taken from the literature [10,13] (Table 2), the corresponding components of the surface tension γ_S^{LW}, γ_S^+ and γ_S^- for fluorites Ia, Ib, IIb, IIIa and IIIb were obtained for those four groups of three liquids. The average values are shown in Table 3. For fluorite IIa there are only two possibilities for calculating the γ_S^{LW}, γ_S^+ and γ_S^- components, assuming that its contact angle for water is strictly equal to zero.

Table 2
Values of liquid surface tension components (mJ m^{-2}) taken from the literature [10,13]

Liquid	γ_L^{LW}	γ_L^+	γ_L^-	γ_L
Water	21.8	25.5	25.5	72.8
Glycerol	34	3.92	57.4	64
Formamide	39	2.28	39.6	58
Diiodomethane	50.8	0.72	0	50.8
Bromoform	41.5	1.72	0	41.5

The results of the calculations show that for a given fluorite (in most cases) there is good agreement between the values of γ_S^{LW}, γ_S^+ and γ_S^- obtained from different groups of liquids.

For fluorite plates Ib and IIb (dried at 110°C) the contribution of the γ_S^+ and γ_S^- components to the surface tension is very small (Table 3). If both components are equal to zero, Eq. (5) may be rewritten as

$$\gamma_S^{LW} = \frac{[\gamma_L(\cos\theta_L + 1)]^2}{4\gamma_L^{LW}} \qquad (6)$$

Therefore for fluorite Ib, for example, the γ_S^{LW} values obtained from the contact angle of a single liquid were calculated from Eq. (6) on the assumption that γ_S^+ and γ_S^- are equal to zero. The calculations were made from Eq. (6) for water, glycerol, formamide, diiodomethane and bromoform, using the measured contact angle values (Table 1) and the literature data of γ_L^{LW} [10,13] (Table 2). The resulting values after application of Eq. (6) are presented in Table 3. The γ_S^{LW} values obtained from

Eq. (6) are a few millijoules per square metre higher than those from Eq. (5). Of course, the γ_S^{LW} values calculated from the contact angle data for polar liquids are slightly higher than those from the apolar liquids.

From Table 3 it can also be seen that for fluorites Ia, IIa, IIIa and IIIb the values of γ_S^+ are lower than those of γ_S^-. For fluorites Ib and IIb, nearly the same values of γ_S^{LW}, γ_S^+ and γ_S^- are observed.

Discussion

Fluorite is partially soluble in water. The "dry" fluorite should be hydrophobic and its surface tension should result only from Lifshitz–van der Waals intermolecular interactions. This characteristic of fluorite is confirmed by the values of γ_S^{LW}, γ_S^+ and γ_S^- obtained for fluorite Ib. For this sample (dried at 110°C before contact angle measurements), the γ_S^+ and γ_S^- values are negligible (Table 3). However, the values of γ_S^{LW} calculated from Eq. (5) are slightly lower than those calculated from Eq. (6), on the assumption that the acid–base interactions at the fluorite–liquid interface are absent. The largest difference is observed between the γ_S^{LW} value determined from Eq. (6) using θ_W and γ_S^{LW} values obtained from Eq. (5). This indicates that ion–dipole interactions can play a particular role in the fluorite–water interfacial tension. This conclusion is confirmed by the observation of the water drop in the time of contact angle measurement. For the system "dry" fluorite–water-drop–

Table 3
Values of the Lifshitz–van der Waals (γ_S^{LW}), electron-acceptor (γ_S^+) and electron-donor (γ_S^-) components of the fluorite surface tension calculated from Eqs. (5) and (6)

Fluorite	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}
Ia	33.49 ± 0.50	0.080 ± 0.073	6.68 ± 0.86	1.46 ± 0.71
Ib	36.26 ± 0.51	0.029 ± 0.014	0.022 ± 0.007	0.05 ± 0.01
IIa	25.68 ± 2.26	6.13 ± 0.78	52.70 ± 0.69	35.95 ± 2.52
IIb	36.30 ± 0.71	0.182 ± 0.127	0.045 ± 0.052	0.18 ± 0.15
IIIa	28.78 ± 1.88	1.22 ± 0.47	30.17 ± 2.08	12.13 ± 2.21
IIIb	33.72 ± 0.25	0.51 ± 0.04	1.90 ± 0.06	1.97 ± 0.05

W, 40.47; G, 39.32; F, 38.93; D, 36.04; B, 37.07; these are the W, G, F, D and B values of γ_S^{LW} for fluorite Ib calculated from Eq. (6) using contact angles for water, glycerol, formamide, diiodomethane and bromoform respectively.

air, the contact angle decreases with the time of contact between water drop and fluorite surface. For the calculations of the average value of θ_w (Table 1), the first measured value for each water drop was used.

The surface of fluorite can have many defects and some of them are able to be saturated with water, according to the following equations:

$$-F^- + H_2O = -F(H_2O)^- = -FH + OH^- \qquad (7)$$

$$-Ca^+ + H_2O = -Ca(H_2O)^+ = -CaOH + H^+ \quad (8)$$
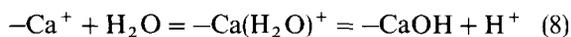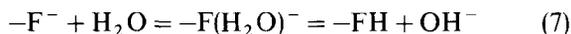
Thus, after a long time of contact between the fluorite surface and water molecules, the surface becomes hydrated. Therefore, for fluorite Ia (dried at only 50°C before contact angle measurements) lower values of γ_S^{LW} and higher values of γ_S^- than for fluorite Ib are observed (Table 3). It is interesting to emphasize that the γ_S^+ values for fluorite Ia are nearly the same as for fluorite Ib and can be negligible. These facts indicate that electron-acceptor interactions of hydrated water molecules are compensated for by those of the F^- ion. It also means that the F^- ion is more hydrated than the $-Ca^+$ ion and therefore a higher value of γ_S^- is observed for fluorite Ia. This is in accordance with an earlier study dealing with the zeta potential for the fluorite–water system [14]. After 10 min of contact between fluorite and water, the sign of the zeta potential was negative at pH values higher than 2. The hydration process does not change the sign of the interactions but only their magnitudes [8].

Treatment of the fluorite surface by HF aqueous solution causes it, after washing and drying at 50°C (fluorite IIa), to become hydrophilic. Water and formamide spread completely over the fluorite plate IIa. This results from the increase in the acid–base intermolecular interactions at the fluorite–polar liquid interface and the decrease in the γ_S^{LW} component. The γ_S^+ and γ_S^- values for fluorite IIa are several times higher than for fluorite Ia, Ib and IIb. In the case of fluorite IIa the value of γ_S^- is also higher than the γ_S^+ value. This proves that

according to Eq. (7) the fluorite surface becomes strongly hydrated.

After fluorite II is dried at 110°C, its surface tension is similar to that of fluorite Ib, which suggests that almost all water molecules are removed from the fluorite surface.

Treatment of a fluorite plate with aqueous $Ca(OH)_2$ solution also causes an increase in surface hydration, but one that is lower than that after treatment of the surface with aqueous HF solution. Water and formamide do not spread over the fluorite IIIa surface completely. Further, compared to the "dry" fluorite surface, a smaller decrease in γ_S^{LW} and smaller increases in γ_S^+ and γ_S^- than for fluorite IIa are observed. However, the drying of fluorite III at 110°C does not cause the complete removal of water molecules from the surface, as shown by the fact that the γ_S^{LW} value for fluorite IIIb is lower and the γ_S^- and γ_S^+ values are higher than those for fluorite Ib or IIb. In this case the influence of CO_2 cannot be excluded.

On the basis of the facts presented above, we can state that fluorite is a hydrophobic mineral but, in the presence of water, hydration occurs, giving rise to polar (acid–base) interactions at the fluorite–water interface.

Acknowledgement

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