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Components of surface free energy of galena

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Measurements of the contact angle for water, diiodomethane, bromoform and 1,1,2,2-tetrabromoethane on non-oxidized and oxidized surfaces of galena were made. Using the results obtained, the "geometric mean" approach, and the long-range and short-range interactions approaches, the dispersion and non-dispersion, and Lifshitz–van der Waals and acid–base components of the surface free energy of galena were determined and compared with those calculated from adsorption isotherms of *n*-octane and *n*-propanol. On the basis of the measurements and calculations it was found that the surface free energy of galena depends on its degree of oxidation and arise mainly from London's and acid–base intermolecular interactions. It was also found that values of the dispersion and non-dispersion components of galena surface free energy determined from the contact angle assuming that a film is present around the water and diiodomethane drops, are close to those obtained from adsorption isotherms of *n*-octane and *n*-propanol.

1. Introduction

Many studies have been carried out dealing with surface free energy of solids over the last 30 years. On the basis of these studies, not only the total surface free energy but also its dispersion and non-dispersion components have been determined, especially for low energetic solids [1–8].

Recently, van Oss *et al.* [9–12] have considered the surface free energy of liquids and solids as resulting from Lifshitz–van der Waals, electron-donor and electron-acceptor intermolecular interactions. The knowledge of the surface free energy of a mineral may be useful to explain its mechanism of enrichment. From the practical point of view, the flotation process is very important. In it, the differences between the values of adhesion of water and air bubbles to the surface of the mineral and gangue play an important role. Adhesion depends on the kind and magnitude of intermolecular interactions acting across the interface of the two phases which are in contact. There is a direct relationship between work of adhesion and the surface free energy of the contacting phases.

Determination of the surface free energy of sulphide minerals encounters additional difficulties, because their surface properties are strongly influenced by humidity and oxygen. As a consequence of water and oxygen interactions with the surface of the sulphide mineral, complicated changes of the structure and composition of the surface layer of the mineral take place [13–16], the result being that surface hydroxides, sulphates, sulphites, thiosulphates and carbonates of metals, as well as elemental sulphur, can be formed [13–16]. These compounds influence both the kind and magnitude of the forces interacting at the surface of sulphides, which leads to changes of the components of the surface free energy of the sulphide mineral. The high dependence of sulphide minerals on the environmental conditions in which they were formed and are present, delimits the possibility of determining their surface free energy exactly. Methods used for the determination of the surface free energy of a mineral are usually based on measurements of the zeta potential [17], adsorption [18] and contact angles [1–8], but in the case of the sulphide minerals, very strict experimental conditions should be used in order to control surface oxidation. In any case, the interpretation of the results is very strenuous and different theoretical approaches made more than one explanation possible. There are a few studies in the literature dealing with surface free energy of sulphide minerals [17, 18]. These studies, however, do not treat the components of the surface free energy of galena and their changes under the influence of oxidation processes directly. Therefore, the main purpose of this work was the determination of the surface free energy components of galena from contact angles measured under different experimental conditions.

2. Experimental procedure

Contact angles were measured at 20 ± 0.1 °C by the sessile drop method [19], using a microscope

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goniometer system at ×25 magnification. The measurement error was ± 1°. Contact angles of galena originating from mineralogical specimens (Olkusz, Poland) were measured for the following liquids: doubly distilled water, diiodomethane (pure, Lachema Brno, Czechoslovakia), 1,1,2,2-tetrabromoethane (pure, Aldrich-Europe, Belgium) and bromoform (p.a. Poch Gliwice, Poland).

A lump of the mineralogical specimens of galena was cut into pieces 5 mm × 10 mm × 5 mm, then these pieces were polished with a series of emery papers (carborundum grit from 400–00). The polishing was performed slowly, by hand, to avoid local overheating and oxidation. The final polishing was made under water until reflecting surfaces were obtained. Then, the pieces were washed several times in doubly distilled water and cleaned in an ultrasonic bath for 20 min. After that the plates were dried in nitrogen and placed in a desiccator filled with a molecular sieve mixture (0.4 nm + 0.5 nm) for 1 h, or immersed in 3% hydrogen peroxide solution for 15, 30, 45 or 60 min. In the case of the latter, the plates were then washed several times in doubly distilled water and dried in heated air and placed in the desiccator filled with a molecular sieve mixture (0.4 nm + 0.5 nm) for 1 h. For some galena plates the final polishing was made with a flannel. The plates thus prepared were then stored in the desiccator.

Contact angles were measured in the galena–liquid drop–air system. The measurements were carried out in the measuring chamber filled with a vapour of a given liquid. The plate of galena was placed in the chamber and after 30 min a liquid drop of 2 mm^3 volume was very carefully settled on the surface of the plate and the contact angle immediately read on both sides. In this way contact angles for water, diiodomethane, bromoform, and 1,1,2,2-tetrabromoethane on "bare" and oxidized surfaces of galena were measured.

For any given system studied, at least ten polished plates of galena were used.

3. Results and discussion

The values of contact angles obtained in the galena–liquid drop–air system are presented in Table I. As the oxidation of the surface increases, i.e. as the time of immersion of the galena plate in 3% H_2O_2 solution (before measurements) increases from 0–60 min, the contact angle values for water, 1,1,2,2-tetrabromoethane, bromoform and diiodomethane decrease by about 40°, 18°, 26° and 7°, respectively.

TABLE I Values of contact angle for water, θ_W, diiodomethane, θ_D, bromoform, θ_B, and 1,1,2,2-tetrabromoethane, θ_T, on the galena surface

Oxidization time (min)	θ_W (deg)	θ_D (deg)	θ_B (deg)	θ_T (deg)
0	82.3	46.4	26.3	41.4
15	62.6	42.6	11.8	33.3
30	53.1	40.9	0.0	28.0
45	46.0	41.2	0.0	27.9
60	41.6	39.5	0.0	23.9

To explain the observed changes of the contact angle values, let us conduct calculations of the surface free energy of galena on the basis of Young's equation. This equation for the galena–liquid drop–air system can be expressed as

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

where γ_S is the surface free energy of galena, γ_{SL} is galena–liquid interfacial free energy, γ_L is the liquid surface tension, Πe_L is the film pressure of the liquid and θ_L is the contact angle. Dividing the surface free energy of galena and liquid into two components (dispersion, γ^d, and non-dispersion, γ^n [1–5]) and expressing γ_{SL} as a function of the geometric mean of dispersion [1–8] and non-dispersion [3, 4, 8] intermolecular interactions, we obtain from Equation 1

$$\gamma_L \cos\theta_L = -\gamma_L + 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^n \gamma_L^n)^{1/2} - \Pi e_L \tag{2}$$

where γ_S^d, γ_S^n, γ_L^d and γ_L^n are dispersion, γ^d, and non-dispersion, γ^n, components of the surface free energy of galena, γ_S, and of a liquid, γ_L. Dispersion and non-dispersion components of the surface free energy of galena can be determined from Equation 2 if contact angles are measured for at least two liquids with different values of the dispersion and non-dispersion components of the surface tension.

From a practical point of view the most suitable pair of liquids to determine the surface free energy of a solid from contact angle values are diiodomethane and water [20]. Equation 2 for diiodomethane and water can be rewritten as

$$\gamma_W \cos\theta_W = -\gamma_W + 2(\gamma_S^d \gamma_W^d)^{1/2} + 2(\gamma_S^n \gamma_W^n)^{1/2} - \Pi e_W \tag{3}$$

$$\gamma_D \cos\theta_D = -\gamma_D + 2(\gamma_S^d \gamma_D^d)^{1/2} + 2(\gamma_S^n \gamma_D^n)^{1/2} - \Pi e_D \tag{4}$$

where W refers to water and D to diiodomethane.

Equations 3 and 4 can be solved against γ_S^d and γ_S^n in four cases: (1) $\Pi e_W = 0$ and $\Pi e_D = 0$, (2) $\Pi e_W = \gamma_S - \gamma_W$ and $\Pi e_D = \gamma_S - \gamma_D$, (3) $\Pi e_W = 0$ and $\Pi e_D = \gamma_S - \gamma_D$, and (4) $\Pi e_W = \gamma_S - \gamma_W$ and $\Pi e_D = 0$. Using the measured contact angle values for water and diiodomethane on galena (Table I), the values of γ_S^d and γ_S^n were calculated from Equations 3 and 4. The other data used for these calculations were taken from the literature [1, 21] (Table II). The calculations were made for the four cases above, but values of γ_S^d and γ_S^n in two cases, namely when $\Pi e_D = 0$ and $\Pi e_W = 0$, and $\Pi e_D = \gamma_S - \gamma_D$ and $\Pi e_W = \gamma_S - \gamma_W$, are worth taking into account in order to discuss the surface free energy of galena. These values are presented in Table III. Values of dispersion and non-dispersion components of the surface free energy of galena calculated from Equations 3 and 4 for $\Pi e_W = 0$ and $\Pi e_D = 0$ are denoted $\gamma_S^d(1)$ and $\gamma_S^n(1)$ and for $\Pi e_W = \gamma_S - \gamma_W$ and $\Pi e_D = \gamma_S - \gamma_D$ as $\gamma_S^d(2)$ and $\gamma_S^n(2)$, respectively.

It appears from Table III that $\gamma_S^d(1)$ values do not depend on oxidation of the galena surface in H_2O_2

TABLE II Values of dispersion, γ_L^d, and non-dispersion, γ_L^n, components of liquid surface tension, γ_L, and water–organic liquid interfacial tension, γ_{WO}, taken from the literature

Liquid	γ_L^d	γ_L^n	γ_L	γ_{WO}	Reference
Water	21.80	51.00	72.80	–	[1]
Diiodomethane	50.42	0.38	50.80	48.50	[20, 23]
Bromoform	40.55	0.95	41.50	40.90	[20, 23]
1,1,2,2-tetrabromoethane	47.92	1.78	49.70	38.80	[20, 23]

TABLE III Values of the dispersion, γ_S^d, non-dispersion, γ_S^n, Lifshitz–van der Waals, γ_S^{LW}, electron-acceptor, γ_S^+, and electron donor, γ_S^-, components of surface free energy of the galena, γ_S, calculated from Equations 3, 4 and 6, respectively

Oxidation time (min)	$\gamma_S^d(1)$ (mJ m^{-2})	$\gamma_S^n(1)$ (mJ m^{-2})	$\gamma_S(1)$ (mJ m^{-2})	$\gamma_S^d(2)$ (mJ m^{-2})	$\gamma_S^n(2)$ (mJ m^{-2})	$\gamma_S(2)$ (mJ m^{-2})	γ_S^{LW} (mJ m^{-2})	γ_S^- (mJ m^{-2})	γ_S^+ (mJ m^{-2})	γ_S^{AB} (mJ m^{-2})	γ_S (mJ m^{-2})
0	34.53	3.76	38.29	116.42	4.34	120.76	34.56	1.31	2.54	3.65	38.21
15	34.81	12.84	47.65	92.34	10.77	103.11	35.25	4.57	8.40	12.39	47.64
30	34.92	18.42	53.34	77.71	13.63	91.34	34.98	8.30	10.16	18.37	53.35
45	34.22	23.14	57.36	66.91	15.96	82.87	34.68	8.95	14.28	22.61	57.29
60	34.78	25.52	60.30	57.33	15.92	73.25	35.07	10.81	14.71	25.22	60.29

solution, but the $\gamma_S^n(1)$ value increases as the oxidation of the galena surface increases. In the second case, $\gamma_S^d(2)$ values decrease and $\gamma_S^n(2)$ values increase with increasing oxidation of galena in H_2O_2 solution. On the basis of these results, we may state that the surface free energy of galena results from dispersion and non-dispersion intermolecular interactions, but nothing can be said about the kind of intermolecular interactions being responsible for the γ_S^n values. This information can be obtained employing one of van Oss *et al.*'s approaches to the surface free energy of solids and liquids [9–12].

Van Oss *et al.* considered the surface free energy as a sum of γ^{LW} and γ^{AB} components, where γ^{LW} results from non-covalent long-range Lifshitz–van der Waals interactions, and γ^{AB} from Lewis acid–base interactions. The γ^{AB} component can be expressed as a function of the geometric mean of γ^+ and γ^- [9–12] parts, originated from electron-acceptor (Lewis acid) and electron-donor (Lewis base) interactions, respectively.

According to van Oss *et al.* [9–12] the interfacial free energy of galena–liquid (γ_{SL}) can be expressed:

$$\gamma_{SL} = [(\gamma_S^{LW})^{1/2} - (\gamma_L^{LW})^{1/2}]^2 + 2[(\gamma_S^+)^{1/2} - (\gamma_L^+)^{1/2}] \times [(\gamma_S^-)^{1/2} - (\gamma_L^-)^{1/2}] \quad (5)$$

Introducing Equation 5 into Equation 1 for $\Pi e_L = 0$, we can write

$$\gamma_L(\cos\theta_L + 1) = 2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + 2(\gamma_S^+\gamma_L^-)^{1/2} + 2(\gamma_S^-\gamma_L^+)^{1/2} \quad (6)$$

To calculate the γ_S^{LW}, γ_S^+ and γ_S^- components of γ_S from Equation 6 it is necessary to carry out contact angle measurements for three different liquids of known γ_L^{LW}, γ_L^+ and γ_L^- values. Using the measured contact angle values for the following pair of liquids: diiodomethane–bromoform, diiodomethane–1,1,2,2-tetrabromoethane and bromoform–1,1,2,2-tetrabromoethane (Table I) on galena, γ_S^{LW} and γ_S^- were calculated from Equation 6. Then, introducing these values and contact angle values for water on galena into Equation 6, and γ_S^+ values were calculated. The values of γ_L^{LW}, γ_L^+ and γ_L^- used in these calculations were taken from the literature [22] in the case of water (Table IV), and for diiodomethane, bromoform and 1,1,2,2-tetrabromoethane were calculated from Equation 5. For calculations, the values of the surface tension of water, diiodomethane, bromoform and 1,1,2,2-tetrabromoethane and the interfacial tension of water-bromoform, water-diiodomethane and water-1,1,2,2-tetrabromoethane were also taken from the literature [23] (Table II) and the assumption that γ_L^- for bromoform, diiodomethane and 1,1,2,2-tetrabromoethane are equal to zero, was made. The average values of γ_S^{LW}, γ_S^+ and γ_S^- calculated from Equation 6 for galena are presented in Table III. As is seen from this table, γ_S^{LW} and γ_S^{AB} values are nearly equal to $\gamma_S^d(1)$ and to $\gamma_S^n(1)$ values, respectively. γ_S^{LW} values do not depend on the oxidation time; however, $\gamma_S^{AB} = 2(\gamma_S^+\gamma_S^-)^{1/2}$ values increase as the degree of oxidation of the galena surface in the 3% H_2O_2 solution increases. It is characteristic that γ_S^+ values are higher than γ_S^-, but they both depend on the degree of oxidization of the galena surface.

According to van Oss *et al.*'s approach [9–12, 22] the γ_S^{LW} component can be treated as a sum of parts due to dispersion, dipole–dipole and induced dipole–dipole interactions. However, from Fowkes approach it results that the dispersion component originates from dispersion (London's) forces. Thus, it can be written

$$\gamma_S^{LW} = \gamma_S^d + \gamma_S^i + \gamma_S^p \quad (7)$$

where i and p refer to induced dipole–dipole and dipole–dipole interactions, respectively.

According to Equation 7, it should be $\gamma_S^{LW} > \gamma_S^d$, but it is found experimentally that γ_S^{LW} and γ_S^d values for these same samples are close, proving that the induced dipole–dipole and dipole–dipole intermolecular interactions play a small role in the surface free

TABLE IV Values of the Lifshitz–van der Waals, γ_L^{LW}, electron acceptor, γ_L^+, and electron donor, γ_L^-, components of liquid surface tension, γ_L taken from the literature

Liquid	γ_L^{LW} (mJ m^{-2})	γ_L^+ (mJ m^{-2})	γ_L^- (mJ m^{-2})	γ_L (mJ m^{-2})	Reference
Water	21.80	25.5	25.5	72.8	[22]
Diiodomethane	50.80	0.72^a	0.00	50.80	[22]
Bromoform	41.50	1.72^a	0.00	41.5^a	[22]
1,1,2,2-tetrabromoethane	49.70	3.13^a	0.00	49.7^a	[22]

^{a} Values calculated from Equation 5.

energy of non-oxidized and oxidized galena. On the basis of this fact it can be stated that the surface free energy of the studied samples arises mainly from London's and acid–base intermolecular interactions.

Such compounds as sulphur, $Pb(OH)_2$, $PbSO_4$, $Pb_2S_2O_3$ and PbO can be present on the galena surface [13–16]. Of course, the values of contact angle measured for water, diiodomethane, bromoform and 1,1,2,2-tetrabromoethane are average values corresponding to the contact angles of the compounds present on the galena surface. The value of the contact angle for water on the non-oxidized galena surface is close to the value obtained for that on the surface of sulphur (80°) [24]. However, the diiodomethane spreads completely on the sulphur surface and in the case of galena the contact angle value for diiodomethane is higher than zero (46.4°). This proves that the surface of non-oxidized galena differs from the surface of sulphur, the ions Pb^{2+} and S^{2-} having their own contribution to the galena surface free energy. This is probably why γ_S^+ and γ_S^{2-} components are higher than zero. Under the influence of H_2O_2, the sulphur and S^{2-} ions can oxidize. As a result of the oxidization process, different kinds of compound are formed on the galena surface, because $\gamma_S^+ > \gamma_S^-$ for a given galena sample what makes the SO_4^{2-} or $S_2O_3^{2-}$ ions dominant on the galena surface possible and hydration of Pb^{2+} ions occur.

Comparing γ_S^d and γ_S^n values calculated here with those obtained from adsorption isotherms of *n*-octane and *n*-propanol on the galena surface [18], we can state that $\gamma_S^d(2)$ and $\gamma_S^n(2)$ are closer to those from adsorption isotherm measurements. For example, for the oxidized surface of galena, the dispersion component is equal to 55 mJ m^{-2} and the non-dispersion component is 14 mJ m^{-2}, and they differ only slightly from those determined from contact angle measurements ($\gamma_S^d(2) = 57.33$ and $\gamma_S^n(2) = 15.92$ mJ m^{-2}). It should be noted that for non-oxidized galena the dispersion component γ_S^d determined from the adsorption isotherm of *n*-octane is 70.2 mJ m^{-2} [18], while $\gamma_S^d(2)$ determined from contact angles is 116.42 mJ m^{-2}. The last value is slightly lower than the dispersion components of the surface free energy of sulphur (124.15 mJ m^{-2} [24]).

4. Conclusion

The calculations presented above, unambiguously suggest that the dispersion and non-dispersion components of the surface free energy of non-oxidized galena are about 35 and 4 mJ m^{-2}, respectively. Oxidization of the galena surface causes an increase of the non-dispersion component, γ_S^n, to 25.5 mJ m^{-2}, while the dispersion component, γ_S^d, does not change its value. These values are obtained using different approaches for the determination of the surface free energy of solids based on Young's equation. This agreement proves that different approaches give good results if the procedures are consequentially applied. The results of the surface free energy of galena mentioned above were obtained assuming that $\Pi e = 0$, but assuming that $\Pi e_L = 0$ we have obtained γ_S^d and γ_S^n values equal to 116.4 and 4.3 mJ m^{-2} for non-oxidized and 57.3 and 15.9 mJ m^{-2} for oxidized galena surfaces, respectively. These values of the surface free energy of galena agree very well with those calculated from the Bangham–Razouk equation with the exception of the γ_S^d value for a non-oxidized galena surface.

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