Components and parameters of synthetic chalcocite surface tension and its wettability by aqueous solution of n-octyl-β-D-glucopyranoside

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Abstract: The measurements of advancing contact angle of water, glycerol, formamide, ethylene glycol, diiodomethane, α-bromonaphthalene, 1,2,3-tribromopropane and aqueous solution of n-octyl-β-D-glucopyranoside (OGP) on unoxidized and oxidized synthetic chalcocite at the temperatures equal to 293, 303 and 313 K were made. Using the obtained contact angle values of the pure liquids the components and parameters of the unoxidized and oxidized synthetic chalcocite surface tension were calculated. For this calculation, different methods based on the Young equation were applied. It follows that the surface tension of both forms of chalcocite does not practically depend on the temperature in the range from 293 to 313 K. Taking into account the calculated values of components and parameters of unoxidized and oxidized chalcocite surface tension their wettability by the aqueous solution of n-octyl-β-D-glucopyranoside was considered. It appeared that wettability of the unoxidized chalcocite by aqueous solution of OGP can be predicted on the basis of the chalcocite surface tension components and parameters.

Keywords: contact angle, wettability, surface tension, chalcocite, n-octyl-β-D-glucopyranoside

1. Introduction

Surface tension of a solid influences on many processes occurring at the solid-gas and solid-liquid interfaces. Among these processes wetting plays a very important role in both industrial and daily life. According to the Young equation (Adamson and Gast, 1997) wetting of the solid expressed by the contact angle depends on the surface tension of solid and liquid as well as that of the solid-liquid interface tension. To show the effect of solid surface tension on the value of contact angle of a given liquid on its surface, the relationship between the solid-liquid interface tension and surface tension of liquid and solid must be known. In the literature, there are many approaches to the solid-liquid as well as liquid-liquid interface tensions (Good and Girilaco, 1960; Fowkes, 1964; Owens and Wendt, 1969; Wu, 1970; van Oss et al., 1987; 1988; van Oss and Good, 1989; Li and Neumann, 1992; Kwok and Neumann, 1999; 2000; Kloubek, 1992; van Oss, 1994;). All these approaches can be divided into two groups. The first, proposed by Fowkes (1964), next developed by Owens-Wendt (1969) and modified by van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) assumes that the solid-liquid or liquid-liquid interface tension depends on the components of solid and liquid surface tension resulting from different kinds of intermolecular interactions. The second one neglects the contribution of the kind of intermolecular interactions to the surface tension of solid and liquid and proves that the solid-liquid interface tension depends only on the total values of surface tension of the phases being in the contact (Li and Neumann, 1992; Kwok and Neumann, 1999; 2000). In the literature, there are many papers in which these two types of approaches to the interface tension are applied for determination of the solid surface tension from the contact angle measurements (van Oss, 1994). However, in the case of the first type of approaches the main problem for their applications to

determine the components and parameters of the solid surface tension from the measurements of contact angle of model liquids is connected with the values of the components and parameters of their surface tension. It is known that the components and parameters of liquid surface tension can be determined by two ways. The first way is based on the measurements of the liquid-liquid interface tension and the other one on the contact angle of the reference solids. In many cases the components and parameters are determined in the mixed first and second ways (Rudawska et al., 2016). In our previous studies, it was shown that the components and parameters of the model liquids determined only from the contact angle measurements on the reference apolar and monopolar solids are more useful for determination of solid surface properties that those obtained from the liquid-liquid interface tension. However, the studies dealing with this problem were limited to some polymers and quartz. From the practical point of view, it is interesting to show the usefulness of the components and parameters of mineral surface tension determined based on the contact angle measurements of the model liquids whose surface tension components and parameters were determined only from the contact angle measured in the reference systems. The surface tension components and parameters of the mineral can be useful for prediction of mineral wetting which is important for its separation from impurities by froth flotation. To change wetting of the useful mineral which is separated by froth flotation, the so-called collector is used. In the case of the sulfide minerals the xantates were used as a collector (Leja, 1982; Roger, 1962). However, it is interesting to know the influence of the sugar surfactant on the hydrophobic-hydrophilic balance of the sulfide mineral and whether it is possible to predict its wetting properties from the components and parameters of the sulfide mineral surface tension. Thus, the aim of our studies was to determine the components and parameters of the synthetic chalcocite surface tension using different methods based on the contact angle measurements and choose the most useful method for prediction of chalcocite wetting by aqueous solution of n-octyl-β-D-glucopyranoside. For these studies the oxidized and unoxidized chalcocite was applied.

2. Experimental

2.1 Materials

Water (W), formamide (F), glycerol (G), ethylene glycol (E), diodomethane (D), α-bromo-naphthalene (B), 1,2,3-tribromopropane (T) and aqueous solution of n-octyl-β-D-glucopyranoside (OGP) were used for the contact angle measurements on the unoxidized and oxidized chalcocite.

Formamide (≥99.5%), glycerol (≥99.5%), ethylene glycol (99.8%), diiodomethane (>99%), α-bromonaphthalene (97%), 1,2,3-tribromopropane (97%) and n-octyl-β-D-glucopyranoside (> 98%) were bought from Sigma-Aldrich. Water was doubly distilled and deionized (Destamat Bi18E). Its resistance was equal to 18.2 Ω. The surface tension of the liquids at 293±0.1K was tested using the Wilhelmy plate and the du Noüy ring method. That at 303 and 313K was calculated on the basis of the temperature coefficient taken from the literature (Poradnik fizykochemiczny, 1997). Synthetic β–chalcocite supplied by the AGH University of Science and Technology, Cracow (Poland) was used as a substitute for the sulfide mineral copper to measure the contact angle. The chalcocite specimens were cut into plates which were polished with of a series of emery papers (Carborundum grit from 400 to 00). Polishing was performed slowly, by hand, to avoid local overheating and oxidization. Final polishing was done under water until reflecting surfaces were obtained. Next, only very smooth plates were chosen and washed several times in doubly distilled and deionized water and placed in an ultrasonic bath for 15 min. Afterwards some of the plates were dried at room temperature and placed in a desiccator filled with a molecular sieve mixture (4 A and 5 A). The other plates were oxidized by immersing them in the 3% hydrogen peroxide solution for 60 min. After being oxidized the plates were washed several times in doubly distilled and deionized water and dried at room temperature.

The aqueous solutions of OGP were prepared using doubly distilled and deionized water. The purity of water was additionally controlled by the surface tension measurements before preparing the solutions. The concentration of OGP was changed from 1×10^{-7} to 5×10^{-2} M.

2.2 Methods

Measurements of the advancing contact angles for the above-mentioned liquids on unoxidized and oxidized chalcocite were made using the sessile drop method, DSA30 measuring system (Krüss) in a thermostated chamber at 293, 303 and 313 K but for the aqueous solution of surfactant only at 293 K. The apparatus chamber was saturated with vapour of the given liquid for which the contact angle was measured placing a cell filled with it a few hours before the measurements. In the case of the organic liquids the water vapour was removed from the apparatus chamber by means of the molecular sieves and then the vessel filled with the measured liquid was introduced into the chamber for a few hours before the contact angle measurements. The contact angle for the given liquid was measured for at least 30 drops and good reproducibility was found. The standard deviation for each set of values was less than 2°. The size of the liquid drop was chosen on the basis of our earlier considerations and it was different for each liquid used.

3. Results and discussion

3.1 Components and parameters of chalcocite surface tension

The contact angle is the parameter of wetting process which depends on the difference between the work of adhesion of a given liquid to the solid surface and its cohesion work. Thus, the work of spreading liquid over the solid surface (W_S) can be expressed by equation (Adamson and Gast, 1997):

$$W_S = \gamma_S - \gamma_L - \gamma_{SL}, \tag{1}$$

where γ_S is the surface tension of solid, γ_L is the surface tension of liquid and γ_{SL} is the solid-liquid interface tension.

As follows from Eq. (1) knowing the surface tension of solid and liquid as well as the solid-liquid interface tension it is possible to predict tendency to wet a given solid by the proper liquid or solution. This is very important in the flotation process. The problem is that only the surface tension of liquid or solution can be measured directly. For determination of the solid surface tension there are only few direct methods for specific solids but they cannot be applied for the minerals separated by froth flotation. In the literature, it is possible to find many indirect methods for solid surface tension determination, among them, those based on the contact angle measurements are the most frequently applied. The contact angle (θ) depends on the surface tension of solid and liquid and the solid-liquid interface tension. This dependence results from the Young equation which has the form (Adamson and Gast, 1997):

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\theta. \tag{2}$$

Determination of solid surface tension on the basis of Eq. (2) requires knowledge of the relationship between the solid-liquid interface tension and the surface tension of solid and liquid. In the literature, there are many different methods to solve the Young equation (Adamson and Gast, 1997). However, among them those proposed by Owens-Wendt (Owens and Wendt, 1969), van Oss et al. (van Oss et al., 1987; 1988; van Oss and Good, 1989; van Oss, 1994) and Neumann et al. (Li and Neumann, 1992; Kwok and Neumann, 1999; 2000) are the most frequently applied. Owens-Wendt based on the Fowkes' concept suggested that the solid-liquid or liquid-liquid interface tensions can be expressed by the following equation (Owens and Wendt, 1969):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_{L1}^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p}, \tag{3}$$

where γ_1, γ_2 are the surface tension of phases 1 and 2, the superscripts d and p refer to the dispersion and polar components of phases 1 or 2 surface tension, respectively.

Owens-Wendt connecting Eqs. (2) and (3) obtained (Owens and Wendt, 1969):

$$\gamma_L(\cos\theta + 1) = 2\sqrt{\gamma_L^d \gamma_S^d} - 2\sqrt{\gamma_L^p \gamma_S^p}. \tag{4}$$

According to Fowkes if the liquid and/or solid surface tension results from the dispersion intermolecular interactions, then Eq. (4) assumes the form (Fowkes, 1964):

22

Physicochem. Probl. Miner. Process., 54(1), 2018, 19-30

$$\gamma_L(\cos\theta + 1) = 2\sqrt{\gamma_L^d \gamma_S^d}. \tag{5}$$

Van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) claimed that the induced dipole-induced dipole, dipole-dipole and induced dipole-dipole interactions constitute an inseparate kind of intermolecular interactions called the Lifshitz-van der Waals one (LW) by them. On the other hand, they suggested that contribution of dipole-dipole and induced dipole-dipole intermolecular interactions to the Lifshitz-van der Waals ones in the condensed phases was lower than 3% (van Oss, 1994). In turn, van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) treated the polar component as the Lewis acid-base one (AB) which was a function of electron-acceptor (+) and electron-donor (-) parameters. Thus, van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) have proposed the following equation for the liquid-liquid or solid-liquid interface tension:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} - 2\sqrt{\gamma_1^+\gamma_2^-} - 2\sqrt{\gamma_1^-\gamma_2^+}. \tag{6}$$

Its introduction to Eq. (2) gives:

$$\gamma_L(\cos\theta + 1) = 2\sqrt{\gamma_L^{LW}\gamma_S^{LW}} + 2\sqrt{\gamma_L^+\gamma_S^-} + 2\sqrt{\gamma_L^-\gamma_S^+}. \tag{7}$$

If the surface tension of solid and/or liquid results from only Lifshitz-van der Waals interactions, then Eq. (7) has the form (van Oss, 1994):

$$\gamma_L(\cos\theta + 1) = 2\sqrt{\gamma_L^{LW}\gamma_S^{LW}}. \tag{8}$$

It should be emphasized that Eqs. (5) and (8) differ only by definition and that the all above presented equations can be applied if behind and under the liquid drop settled on the solid surface a film changing the solid surface tension is not formed and chemical reactions do not take place.

Table 1. The average values of the Lifshitz-van der Waals (γ_{LV}^{LW}) and Lewis acid-base (γ_{LV}^{AB}) components of the water (W), glycerol (G), formamide (F), ethylene glycol (E), diiodomethane (D), a-bromonaphthalene (B) and 1,2,3-tribromopropane (T) surface tension (γ_{LV}) components as well as electron-acceptor (γ_{LV}^+) and electron-donor (γ_{LV}^-) parameters of the acid-base component (γ^{AB}) at the temperature equal to 293, 303 and 313 K taken from literature (Zdziennicka et al., 2017c)

Liquid	Temperature	γ_{LV}	γ_{LV}^{LW}	γ_{LV}^{AB}	γ_{LV}^+	γ_{LV}^-
Water	293	72.8	26.85	45.95	22.975	22.975
	303	71.286	26.85	44.436	22.218	22.218
	313	69.772	26.85	42.922	21.461	21.461
Glycerol	293	64.00	34.00	30.00	9.43	23.87
	303	63.40	34.00	29.40	8.88	24.34
	313	62.80	34.00	28.80	8.48	24.46
Formamide	293	58.00	39.00	19.00	3.67	24.61
	303	57.16	39.00	18.16	3.37	24.44
	313	56.32	39.00	17.32	2.91	25.78
Ethylene glycol	293	48.00	29.00	19.00	4.7	19.2
	303	47.11	29.00	18.11	3.92	20.91
	313	46.22	29.00	17.22	3.45	21.49
Diiodomethane	293	50.80	50.80	0.00	0.00	0.00
	303	49.424	49.424	0.00	0.00	0.00
	313	48.048	48.048	0.00	0.00	0.00
a-Bromonaphthalene	293	44.40	44.40	0.00	0.00	0.00
	303	43.421	43.421	0.00	0.00	0.00
	313	42.442	42.442	0.00	0.00	0.00
1,2,3-Tribromopropane	293	45.40	49.70	0.00	0.00	0.00
	303	44.133	44.133	0.00	0.00	0.00
	313	42.866	42.866	0.00	0.00	0.00

Table 2. The values of the contact angle of water (θ_W), glycerol (θ_G), formamide (θ_F), ethylene glycol (θ_E), diiodomethane (θ_D), *a*-bromonaphthalene (θ_B) and 1,2,3-tribromopropane (θ_T) on the unoxidized and oxidized chalcocite surface at the temperature equal to 293, 303 and 313 K

Type of chalcocite	Temperature	θ_W	θ_G	θ_F	θ_E	θ_D	θ_B	θ_T
unoxidized	293	80.2	66.9	54.8	47.7	46.4	36.2	38.1
	303	78.6	66.1	53.6	45.2	44.0	34.0	35.1
	313	77.0	65.4	52.4	43.4	41.4	31.6	32.0
oxidized	293	40.0	27.0	5.0	0.0	37.3	23.0	26.0
	303	37.6	25.8	0.0	0.0	34.5	19.6	21.9
	313	35.0	24.4	0.0	0.0	31.3	15.2	16.8

Table 3. The average values of the Lifshitz-van der Waals (γ_S^{LW}) and Lewis acid-base (γ_S^{AB}) components of the unoxidized and oxidized chalcocite surface tension (γ_S) components as well as electron-acceptor (γ_S^+) and electron-donor (γ_S^-) parameters of the acid-base component at the temperature equal to 293 K calculated from Eq. (7)

Liquids	Unoxidized chalcocite					Oxidized chalcocite				
	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S
W-G-F	49.1	0.03	2.23	-0.55	48.56	34.70	6.25	20.65	22.71	57.41
W-G-E	64.11	2.45	3.23	5.63	58.48	-	-	-	-	-
W-F-E	15.07	16.82	0.35	4.83	19.90	-		-	-	-
G-F-E	246.5	144.76	14.74	92.38	154.12	-	-	-	-	-
W-G-D	36.26	1.40	1.43	2.83	39.08	40.94	3.23	22.07	16.88	57.82
W-F-D	36.26	1.37	1.46	2.83	39.08	40.94	3.25	22.01	16.92	57.86
W-E-D	36.26	1.35	1.48	2.82	39.08	40.94	0.06	45.38	-3.27	37.68
G-F-D	36.26	1.35	1.51	2.85	39.11	40.94	3.26	21.92	16.92	57.86
G-E-D	36.26	1.29	1.61	2.88	39.14	40.94	9.26	153.69	-75.45	-34.51
F-E-D	36.26	1.39	1.39	2.78	39.04	40.94	30.00	23.26	-52.83	-11.89
W-G-B	36.24	1.40	1.43	2.83	39.07	40.94	3.23	22.07	16.88	57.82
W-F-B	36.24	1.37	1.46	2.83	39.07	40.94	3.25	22.01	16.92	57.86
W-E-B	36.24	1.35	1.48	2.83	39.07	40.94	0.06	45.38	-3.26	37.68
G-F-B	36.24	1.35	1.51	2.86	39.10	40.94	3.26	21.92	16.92	57.86
G-E-B	36.24	1.29	1.61	2.89	39.13	40.94	9.26	153.69	-75.45	-34.51
F-E-B	36.24	1.40	1.39	2.78	39.03	40.94	30.00	23.26	-52.83	-11.89
W-G-T	36.24	1.40	1.43	2.83	39.07	40.92	3.23	22.07	16.90	57.82
W-F-T	36.24	1.37	1.46	2.83	39.07	40.92	3.26	22.01	16.93	57.85
W-E-T	36.24	1.35	1.51	2.86	39.10	40.92	0.06	45.38	-3.24	37.69
G-F-T	36.24	1.35	1.51	2.86	39.10	40.92	3.27	21.91	16.93	57.86
G-E-T	36.24	1.35	1.48	2.83	39.07	40.92	9.25	153.68	-75.39	-34.47
F-E-T	36.24	1.40	1.38	2.78	39.03	40.92	30.02	23.26	-52.86	-11.93
Average	36.25	1.36	1.47	2.83	39.08	40.93	3.25	22.00	16.91	57.85

Determination of components and parameters of the solid surface tension applying the Owens-Wendt (Owens and Wendt, 1969) and van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) methods is possible if we know their exact values for the model liquid surface tension. Of course, these components and parameters depend on the temperature and they should be known to establish wetting properties at different temperatures which is very important from a practical point of view. In the previous papers (Zdziennicka et al., 2017a, b) it was proved that the components and parameters of model liquids determined only on the basis of the contact angle obtained on the model solids were more useful for prediction of wetting process in some systems.

Therefore, the values of components and parameters of model liquids determined only in such a way (Table 1) were used for calculation of the components and parameters of the unoxidized and oxidized chalcocite from the contact angle measurements (Table 2).

Contrary to Owens-Wendt (Owens and Wendt, 1969) and van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) Neumann et al. (Li and Neumann, 1992; Kwok and Neumann, 1999; 2000) suggested that the value of the contact angle of a given liquid on the solid surface depends only on the total surface tension of liquid and solid and contribution of different kinds of intermolecular interactions to the surface tension is insignificant. They proposed the following equation for calculation of the solid surface tension:

$$\frac{\cos\theta+1}{2} = \sqrt{\frac{\gamma_S}{\gamma_L}}\,exp[-\beta(\gamma_L-\gamma_S)^2], \tag{9}$$

where β is the constant which does not depend on the kind of solid and is assumed to be equal to 0.000115 $(m^2/mJ)^2$.

Table 4. The average values of the Lifshitz-van der Waals (γ_S^{LW}) and Lewis acid-base (γ_S^{AB}) components of the unoxidized and oxidized chalcocite surface tension (γ_S) components as well as electron-acceptor (γ_S^+) and electron-donor (γ_S^-) parameters of the acid-base component at the temperature equal to 303 K calculated from Eq. (7)

Liquids	Unoxidized chalcocite					Oxidized chalcocite				
	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S
W-G-F	36.99	1.07	1.79	2.76	39.75	18.43	20.68	18.37	38.98	57.41
W-G-E	34.89	1.59	1.70	3.28	38.18					
W-F-E	35.78	1.37	1.72	3.07	38.84					
G-F-E	35.67	1.40	1.69	3.08	38.75					
W-G-D	36.53	1.17	1.77	2.88	39.41	41.11	3.16	22.35	16.8	57.91
W-F-D	36.53	1.17	1.77	2.88	39.41	41.11	2.77	23.41	16.12	57.23
W-E-D	36.53	1.19	1.75	2.88	39.41	41.11	0.01	43.81	-1.52	39.60
G-F-D	36.53	1.18	1.76	2.88	39.4	41.11	2.55	25.27	16.04	57.16
G-E-D	36.53	1.21	1.69	2.86	39.39	41.11	4.04	120.93	-44.21	-3.1
F-E-D	36.53	1.12	1.96	2.96	39.49	41.11	60.01	133.13	-178.8	-137.7
W-G-B	36.31	1.22	1.76	2.93	39.25	40.94	3.22	22.32	16.95	57.89
W-F-B	36.31	1.23	1.75	2.93	39.25	40.94	2.84	23.37	16.28	57.23
W-E-B	36.31	1.24	1.74	2.94	39.25	40.94	0.01	43.78	-1.3	39.65
G-F-B	36.31	1.23	1.74	2.93	39.24	40.94	2.61	25.22	16.22	57.16
G-E-B	36.31	1.26	1.69	2.91	39.23	40.94	3.98	120.93	-43.87	-2.92
F-E-B	36.31	1.19	1.89	2.99	39.31	40.94	60.39	133.56	-179.6	-138.6
W-G-T	36.47	1.18	1.77	2.89	39.36	41.01	3.19	22.33	16.89	57.90
W-F-T	36.47	1.19	1.76	2.89	39.37	41.01	2.81	23.39	16.22	57.23
W-E-T	36.47	1.20	1.74	2.90	39.37	41.01	0.01	43.79	-1.38	39.63
G-F-T	36.47	1.19	1.75	2.89	39.36	41.01	2.58	25.24	16.15	57.16
G-E-T	36.47	1.22	1.69	2.87	39.35	41.01	4.00	120.93	-43.99	-2.99
F-E-T	36.47	1.14	1.94	2.97	39.44	41.01	60.25	133.4	-179.3	-138.3
Average	36.44	1.20	1.77	2.91	39.35	41.02	3.19	22.33	16.88	57.90

The calculated values of the Lifshitz-van der Waals and acid-base components and electron-acceptor and electron-donor parameters of the unoxidized and oxidized chalcocite at the temperatures 293, 303 and 313 K calculated from Eq. (7) are presented in Tables 3 – 5, respectively. The values of the dispersion and polar components of the unoxidized and oxidized chalcocite surface tension calculated from Eq. (4) are presented in Tables 6 and 7 and the total surface tension calculated from Eq. (9) in Table 8. In order to calculated components and parameters of unoxidized and oxidized chalcocite surface tension from Eqs. (4) and (7) all possible liquid systems were applied. It means that in the case

of Eq. (4) the contact angles of different pairs of liquids were taken into account. In turn, to solve equation (7) against the Lifshitz-van der Waals component and two parameters, the contact angle of three different liquids was measured.

Table 5. The average values of the Lifshitz-van der Waals (γ_S^{LW}) and Lewis acid-base (γ_S^{AB}) components of the unoxidized and oxidized chalcocite surface tension (γ_S) components as well as electron-acceptor (γ_S^+) and electron-donor (γ_S^-) parameters of the acid-base component at the temperature equal to 313 K calculated from Eq. (7)

Liquids	Unoxidized chalcocite					Oxidized chalcocite				
	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S
W-G-F	34.73	1.44	2.05	3.44	38.17					
W-G-E	38.22	0.70	2.18	2.46	40.68					
W-F-E	37.45	0.83	2.16	2.67	40.12					
G-F-E	37.56	0.80	2.19	2.65	40.21					
W-G-D	36.79	0.96	2.12	2.86	39.66	41.31	3.07	22.65	16.67	57.98
W-F-D	36.79	0.96	2.14	2.86	39.65	41.31	2.27	25.04	15.07	56.38
W-E-D	36.79	0.95	2.15	2.86	39.65	41.31	0.03	44.68	-2.33	38.98
G-F-D	36.79	0.95	2.15	2.87	39.66	41.31	1.88	29.20	14.82	56.13
G-E-D	36.79	0.93	2.21	2.87	39.66	41.31	3.46	118.63	-40.52	0.79
F-E-D	36.79	0.99	2.00	2.81	39.6	41.31	45.34	111.42	-142.1	-100.8
W-G-B	36.38	1.05	2.11	2.98	39.36	40.97	3.18	22.61	16.97	57.94
W-F-B	36.38	1.04	2.12	2.98	39.36	40.97	2.37	25.00	15.40	56.37
W-E-B	36.38	1.03	2.14	2.97	39.35	40.97	0.02	44.65	-1.91	39.06
G-F-B	36.38	1.04	2.13	2.98	39.36	40.97	1.98	29.14	15.18	56.15
G-E-B	36.38	1.01	2.22	2.99	39.37	40.97	3.35	118.69	-39.88	1.09
F-E-B	36.38	1.10	1.90	2.89	39.27	40.97	45.91	112.01	-143.4	-102.4
W-G-T	36.60	1.00	2.12	2.92	39.52	41.06	3.15	22.62	16.89	57.95
W-F-T	36.60	1.00	2.13	2.91	39.51	41.06	2.34	25.01	15.31	56.37
W-E-T	36.60	0.98	2.15	2.91	39.51	41.06	0.02	44.66	-2.01	39.04
G-F-T	36.60	0.99	2.14	2.92	39.52	41.06	1.95	29.15	15.09	56.14
G-E-T	36.60	0.97	2.21	2.93	39.53	41.06	3.38	118.67	-40.04	1.02
F-E-T	36.60	1.04	1.95	2.85	39.45	41.06	45.76	111.86	-143.1	-102.0
Average	26.59	1.00	2.12	2.91	39.50	41.11	3.13	22.63	16.84	57.96

The solution of Eq. (7) against γ_S^{LW}, γ_S^+ and γ_S^- is possible on the basis of contact angle of two groups of liquids. One is based on the contact angle values of three bipolar liquids and the other on that of one apolar and two bipolar liquids. It appeared that for the unoxidized chalcocite at each temperature the values of γ_S^{LW}, γ_S^+ and γ_S^- calculated based on the contact angle of three bipolar liquids depend on the kind of liquid and are different from those calculated from the contact angle of two bipolar and one apolar liquids (Tables 3 – 5). In turn, the values of γ_S^{LW}, γ_S^+ and γ_S^- obtained on the basis of θ values of two bipolar and one apolar liquids are very consistent independently of the type of bipolar and polar liquids. It proved that the values of γ_S^+ and γ_S^- are small and γ_S^+ is insignificantly lower than γ_S^-. This fact suggests that on the unoxidized chalcocite surface copper and sulfur atoms are present or some amounts of water molecules are adsorbed on the chalcocite surface. The great discrepancies between the values of γ_S^{LW}, γ_S^+ and γ_S^- obtained from the contact angle for the three bipolar liquids, as mentioned earlier (Zdziennicka et al. 2017c) results from their great sensitivity to the contact angle. In such a case the accuracy of contact angle value should be to the third decimal point which is impossible to obtain by measurements. It is interesting that the values of dispersion and polar components calculated from Eq. (4) using the contact angle values of one apolar and one polar liquids are similar to those of γ_S^{LW} and γ_S^{AB} ones (Tables 3 – 7). In fact, if for calculation of γ_S^d and

γ_S^p the contact angles of two bipolar liquids are used, then different values of these components were obtained (Tables 6 and 7) for the same reason as mentioned above.

Table 6. Values of the dispersion (γ_S^d) and polar (γ_S^p) components of the unoxidized chalcocite calculated from Eq. (4) at temperature equal to 293, 303 and 313 K

Pair of liquid	293 K			303 K			313 K		
	γ_S^d	γ_S^p	γ_S	γ_S^d	γ_S^p	γ_S	γ_S^d	γ_S^p	γ_S
W-G	38.02	2.47	40.48	36.92	2.82	39.75	35.61	3.25	38.86
W-F	39.58	2.17	41.75	38.73	2.45	41.19	37.96	2.72	40.68
W-E	38.64	2.35	40.98	38.57	2.48	41.06	37.24	2.88	40.12
G-F	40.88	1.76	42.64	40.15	1.96	42.11	39.68	2.08	41.76
G-E	39.73	2.03	41.76	41.23	1.72	42.95	39.58	2.10	41.69
F-E	41.88	1.48	43.36	39.13	2.31	41.44	39.78	2.05	41.83
W-D	36.26	2.83	39.08	36.53	2.91	39.44	36.79	2.98	39.77
G-D	36.26	2.97	39.23	36.53	2.94	39.47	36.79	2.88	39.67
F-D	36.26	3.46	39.72	36.53	3.35	39.87	36.79	3.21	40.01
E-D	36.26	3.14	39.4	36.53	3.19	39.72	36.79	3.04	39.83
W-B	36.24	2.83	39.07	36.31	2.96	39.27	36.38	3.07	39.45
G-B	36.24	2.98	39.22	36.31	3.01	39.32	36.38	3.00	39.39
F-B	36.24	3.47	39.71	36.31	3.44	39.76	36.38	3.40	39.78
E-B	36.24	3.15	39.39	36.31	3.27	39.59	36.38	3.20	39.58
W-T	36.24	2.83	39.07	36.47	2.92	39.39	36.60	3.02	39.62
G-T	36.24	2.98	39.22	36.47	2.96	39.43	36.60	2.94	39.54
F-T	36.24	3.47	39.71	36.47	3.37	39.84	36.60	3.30	39.90
E-T	36.24	3.15	39.39	36.47	3.21	39.69	36.60	3.11	39.71
Average	36.25	3.11	39.36	36.44	3.13	39.57	36.59	3.10	36.69

The values of the unoxidized chalcocite surface tension calculated from the Neumann et al. (Li and Neumann, 1992; Kwok and Neumann, 1999; 2000) equation depend on the kind of the liquids for each the contact angle was used. However, in the case of apolar liquids the values of the total surface tension obtained from Eq. (9) are close to γ_S^{LW}. The lack of consistence of the results obtained from Eq. (9) suggested on one hand that the contact angle values depend not only on the surface tension of solid and liquid but also on the contribution of different kinds of intermolecular interactions to the surface tension. On the other hand, β in Eq. (9), which was established on the basis of the systems including polymers (Li and Neumann, 1992; Kwok and Neumann, 1999; 2000), is not proper for chalcocite. It is also possible that β depends on the kind of the solid and liquid. Calculations of the components and total surface tension independently of the applied method indicate that in the temperature range from 293 to 313 they are almost constant. However, there are some discrepancies between the parameters in this range of temperature. It may be worth emphasizing that the total surface tension of the unoxidized chalcocite is close to that of polymethyl methacrylate (Zdziennicka et al., 2017a).

In the case of the oxidized chalcocite the contact angle values for all studied liquids are lower than those for the unoxidized one (Table 2) and for formamide at 293 and 313 K and ethylene glycol at each temperature are equal to zero. Therefore, all calculations based on the contact angle equal to zero are not real because we do not know whether in these cases the spreading coefficient is equal to zero. If it is negative, then the Young equation is not applicable. For this reason, we do not present the results obtained from Eq. (7) on the basis of the contact angle of three bipolar liquids but those calculated from the contact angle of two bipolar and one apolar liquids. However, the results obtained from the contact angle for three liquids including formamide, ethylene glycol and apolar liquid should be treated as an example that probably for formamide and ethylene glycol the spreading coefficient (the work of spreading) is negative. Taking into account only the values of γ_S^{LW}, γ_S^+ and γ_S^- obtained from the contact angle of water, glycerol and all apolar liquids it can be stated that these values are similar

to the quartz surface tension and electron-donor parameter is close to that of water surface tension (Tables 1 and 3 - 5). This suggest that probably the oxygen and –OH groups decide about the magnitude of oxidized chalcocite surface tension. Similar to the unoxidized chalcocite the components of oxidized chalcocite surface tension do not depend on the temperature in the studied range, however, there are insignificant differences among the γ_S^+ and γ_S^- values. In the case of the oxidized chalcocite, there is smaller agreement between the dispersion and polar components as well as the Lifshitz-van der Waals and acid-base components of the chalcocite surface tension. It is interesting that the surface tension of the oxidized chalcocite calculated from Eq. (9) on the basis of the contact angle of water and glycerol is nearly the same as those calculated from Eq. (7) based on the contact angle of water, glycerol and apolar liquids. On the other hand, the total surface tension calculated from Eq. (9) based on the contact angle of apolar liquid is close to γ_S^{LW} component (Tables 3 - 5 and 9).

Table 7. Values of the dispersion (γ_S^d) and polar (γ_S^p) components of the oxidized chalcocite calculated from Eq. (4) at temperature equal to 293, 303 and 313 K

Pair of liquid	293 K			303 K			313 K		
	γ_S^d	γ_S^p	γ_S	γ_S^d	γ_S^p	γ_S	γ_S^d	γ_S^p	γ_S
W-G	27.17	30.24	57.41	26.23	31.38	57.62	25.5	32.41	57.91
W-F	32.29	26.42	58.71	30.98	27.63	58.61	29.37	29.16	58.54
W-E	10.53	49.04	59.57	9.28	52.06	61.34	8.20	55.08	63.28
G-F	36.79	21.07	57.87	34.87	22.66	57.52	32.31	25.04	57.34
G-E	0.04	127.07	127.11	0.04	128.48	128.53	0.04	129.78	129.82
F-E	132.29	10.23	142.52	137.22	14.09	151.30	139.36	17.48	156.84
W-D	40.94	21.09	62.03	41.11	21.15	62.27	41.31	21.19	62.50
G-D	40.94	17.95	58.89	41.11	17.76	58.88	41.31	17.61	58.92
F-D	40.94	16.92	57.86	41.11	16.13	57.25	41.31	15.12	56.43
E-D	40.94	9.65	50.59	41.11	8.74	49.85	41.31	7.83	49.13
W-B	40.94	21.09	62.03	40.94	21.25	62.19	40.97	21.38	62.35
G-B	40.94	17.95	58.89	40.94	17.88	58.83	40.97	17.85	58.82
F-B	40.94	16.92	57.86	40.94	16.29	57.23	40.97	15.43	56.40
E-B	40.94	9.65	50.59	40.94	8.84	49.78	40.97	8.02	48.99
W-T	40.92	21.10	62.02	41.01	21.21	62.22	41.06	21.34	62.39
G-T	40.92	17.96	58.88	41.01	17.84	58.84	41.06	17.79	58.84
F-T	40.92	16.94	57.86	41.01	16.23	57.24	41.06	15.35	56.41
E-T	40.92	9.66	50.59	41.01	8.80	49.81	41.06	7.97	49.03
Average	40.93	18.66	59.59	41.02	19.52	60.54	41.11	19.53	60.64

Table 8. The values of the unoxidized and oxidized chalcocite surface tension (γ_S) calculated from Eq. (9) at temperature equal to 293, 303 and 313 K

Liquid	γ_S of unoxidized chalcocite			γ_S of oxidized chalcocite		
	293 K	303 K	313 K	293 K	303 K	313 K
W	34.76	34.75	34.73	59.21	59.21	59.21
G	36.79	36.82	36.80	57.72	57.70	57.67
F	39.11	39.11	39.08	57.79	57.17	56.30
E	34.93	35.33	35.39	48.00	47.11	46.22
D	37.71	37.70	37.70	41.72	41.69	41.70
B	36.74	36.70	36.67	41.05	41.00	41.00
T	36.86	36.91	36.90	41.10	41.08	41.08

3.2 Wettability of chalcocite by aqueous solution of OGP

As follows from Fig. 1 the shape of the isotherm of contact angle of aqueous solution of OGP on the unoxidized chalcocite is similar to the isotherm of surface tension of this solution (Mańko et al., 2014). However, in the case of the oxidized chalcocite the maximum on the isotherm of the contact angle of OGP solution is observed. The maximal value of the contact angle is higher than 90°. This means that adsorption of OGP on the oxidized chalcocite surface causes its hydrophobization to the extent comparable to that of ethyl xantate. If the components and parameters of the chalcocite surface tension have important meaning in practice, then it is possible to explain the changes of the contact angle of aqueous solutions of OGP on the unoxidized and oxidized chalcocite surfaces.
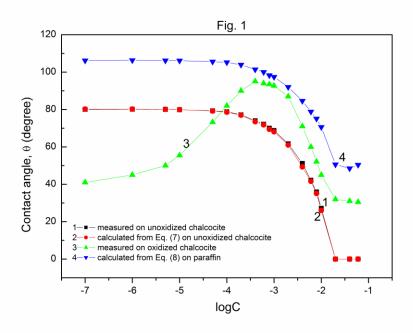

Fig. 1. A plot of contact angle vs. the logarithm of the OGP concentration. Curves 1 (■) and 3 (▲) correspond to the values of the measured contact angle of OGP aqueous solution on the unoxidized and oxidized chalcocite, respectively, curve 2 (●) corresponds to the values of contact angle of OGP aqueous solution calculated from Eq. (7) on the unoxidized chalcocite and curve 4 (▼) corresponds to the values of the contact angle of OGP aqueous solution calculated from Eq. (8) on paraffin

In the previous paper (Zdziennicka et al., 2017a) it was established that the γ_S^{LW} value of water surface tension equal to 26.85 mN/m is useful for prediction of wettability of hydrophobic solids by the aqueous solution of surfactants and their mixtures. The value equal to 26.85 mN/m is close to that of the surface tension of many surfactants oriented by the hydrophobic part towards another phase (Zdziennicka et al., 2017c). Thus, the changes of the surface tension of the aqueous solution of OGP as a function of its concentration can be associated only with the decrease of the acid-base component of this tension. If it is assumed that similar to the surface tension of water the electron-acceptor and electron-donor parameters of the OGP solution have the same values, then it is possible to calculate the contact angle of aqueous solution of OGP from Eq. (7) on the basis of the components and parameters of the unoxidized chalcocite surface tension. Taking into account the average values of γ_S^{LW}, γ_S^+ and γ_S^- as well as the surface tension of the aqueous solution of OGP the contact angle of this solution on the unoxidized chalcocite surface was calculated from Eq. (7). There proved to be excellent agreement between the measured and calculated values of the contact angle (Fig. 1). This agreement indicates that the Lifshitz-van der Waals intermolecular interactions play a main role in adsorption of OGP from the solution on the unoxidized surface of chalcocite. A quite different mechanism of OGP molecules adsorption is found in the case of the chalcocite oxidized surface. As mentioned above the maximum on the isotherm of the contact angle is observed. If it is assumed that on the oxidized

chalcocite surface the OGP molecules are oriented by the hydrophilic part toward the chalcocite surface, then the hydrophobic properties of chalcocite should be intensified. The intensification probably occurs up to the saturation of the OGP monolayer on the oxidized chalcocite in which its molecules are oriented by the hydrophobic part toward solution. To confirm this idea hypothetical contact angle values of the OGP solution on paraffin surface were calculated from Eq. (8). According to Fowkes (Fowkes, 1964) the surface tension of paraffin was assumed to result only from the Lifshitz-van der Waals intermolecular interactions being equal to 25.5 mN/m. In fact, as mentioned above the Lifshitz-van der Waals component of the aqueous solution of OGP was assumed to be constant in the range of studied OGP concentration and is equal to the Lifshitz-van der Waals component of water surface tension (26.85 mN/m). The calculated values of the contact angle of OGP solution on paraffin approximate the maximal measured value at the OGP concentration close to the first concentration at which its saturated monolayer at the water-air interface is formed (Mańko et al., 2014). From this concentration, the changes of hypothetical contact angle as a function of OGP concentration are parallel to those measured ones. This fact suggests that the OGP molecules are oriented in the saturated monolayer at the chalcocite-water interface by the hydrophobic part toward the water phase and that a saturated monolayer is formed at the same concentration as that at the water-air interface.

The presented calculations indicate that the components and parameters of the chalcocite surface tension calculated from the corrected by us values of components and parameters of model liquids surface tension applied in the van Oss at al. method (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) allow to predict the contact angle of surfactant solution on the unoxidized chalcocite surface and to explain the mechanism of adsorption of the surfactants on the oxidized chalcocite surface.

4. Conclusions

From our studies, the following conclusions can be drawn:

1. Unoxidized chalcocite has hydrophobic while oxidized one hydrophilic character.
2. The van Oss et al. method of the calculation of the component and parameters of the solid surface tension provides better information about surface properties than the others.
3. The surface tension components and parameters of unoxidized and oxidized chalcocite surface tension are almost constant in the temperature range from 293 to 313 K.
4. The surface tension values of both forms of chalcocite calculated from the Neumann et al. equation depend on the type of liquid for which the contact angle was measured.
5. For the unoxidized chalcocite the van Oss et al. and Owens-Wendt methods give practically the same results.
6. The contact angle of aqueous solutions of OGP on the unoxidized chalcocite can be predicted based on the basis of the components and parameters of the chalcocite surface tension, the surface tension of OGP solution and the Lifshitz-van der Waals component of water surface tension was equal to 26.85 mN/m.

The OGP hydrophobizes the oxidized surface of chalcocite to the extent comparable to that of ethyl xantate.

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