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MEASUREMENT OF CONTACT ANGLE OF COPPER-BEARING SHALES USING THE CAPTIVE BUBBLE METHOD

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Abstract: This paper describes the measurement of contact angle of the natural surface of copper-bearing shales immersed in solutions of selected reagents of various concentrations using captive bubble method. It demonstrates that the copper-bearing shales coming from Legnicko-Głogwski Copper Region develop natural hydrophobic properties in surfactant (frother) solutions and its hydrophobicity decreases from 82^0 contact angle in distilled water, 78^0 in C_4E_1 solutions, 76^0 in C_4E_2 solutions, to 75^0 in dodecylphenol solutions. These data show that the addition of frother causes a decrease of shale hydrophobicity but it can reduce stability of the thin film between the grain and air bubble. It means that flotation of copper-bearing shales in the presence of frother will only be possible provided specific concentrations.

Key words: contact angle, hydrophobicity, hydrophilicity, flotation

1. INTRODUCTION

Knowledge of physical and chemical processes occurring between liquid and solid body is important from the technology point of view. Measurement of contact angles and determination of interfacial tensions are very important for preparation of new technologies, in which a gas-liquid-solid body system occurs. These matters are important for development of new solutions in many branches of industry.

Depletion of existing copper ore deposits and use of new resources result in occurrence of difficulties in ore concentration and in copper metallurgy process. These difficulties are related with systematic quantity increase of copper-bearing shales, which have mineralogical and flotation properties adversely affecting ore concentra-

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tion process. Flotation of these shales is usually difficult. Łuszczkiewicz and Czechowski (1993) and Łuszczkiewicz (2000) demonstrated in their studies that the flotation of Polish shale-type copper ore, however difficult, is possible using oil. On the other hand, the studies carried out by Drzymała et al. (2002) demonstrated that separation of bituminous shales from copper sulfide-based minerals using diesel oil, C16E23 and dodecyphenol is impossible.

Flotation is a concentration method, in which the difference in wettability of grain surface of individual ingredients is used to separate various grains from the blends. Flotation efficiency depends primarily on hydrophobicity, which is usually expressed by contact angle (Adamson, 1967). Separation of mineral blends consists in lifting by air bubbles of the grains, which have low water or aqueous surfactant solution wettability. Four basic conditions have to be fulfilled to lift the grains of hydrophobic material to the surface by air bubbles and turn them into a foam. First, a collision of mineral grain with air bubble has to occur, and, subsequently, water film formed between air bubble and mineral grain has to break. A proper adhesion force has to develop between the grain and the air bubble, which will cause formation of grain-air bubble aggregate, density of which has to be lower than the density of liquid in which the flotation process runs (Drzymała, 2007). On the other hand, mineral grains of hydrophyllic properties do not form grain attachment with air bubbles and fall, as a precipitate, to the bottom (Laskowski and Łuszczkiewicz, 1989).

Contact angle is a measure of mineral hydrophobicity. The value of this angle decides whether a grain will form a grain attachment with a bubble, and, therefore, the flotation result depends, among the other things, on the value of contact angle of minerals being floated. A contact angle is an angle between the plane of a solid body and a tangent line at the point of contact of solid, liquid and gaseous phase measured either through a liquid or a gaseous phase (Ratajczak and Drzymała, 2003). Fig1 illustrates measurements via liquid phase

In the presented study the captive bubble method was used to determine the contact angle of copper-bearing shales. In this method, the angle of contact between air bubble and mineral grain immersed in water or in aqueous surfactant solution is measured directly. Care should be taken to prevent adherence of air bubble to grain edge during the measurement, because otherwise, the measurement results may be corrupted. Result abnormality may be caused by different hydrophobicity of grain edges or by acting of additional forces. To avoid hysteresis of contact angle, the tested surface of a mineral has to be properly polished prior to the measurement. Occurrence of contact angle hysteresis may be recognized by obtaining the value of contact angle measured through liquid phase upon slight increase of air bubble size lower than its value observed upon removal of air from the bubble. The largest and the smallest measured values are called "advancing" and "receding" contact angle, respectively (Drzymała, 2007).

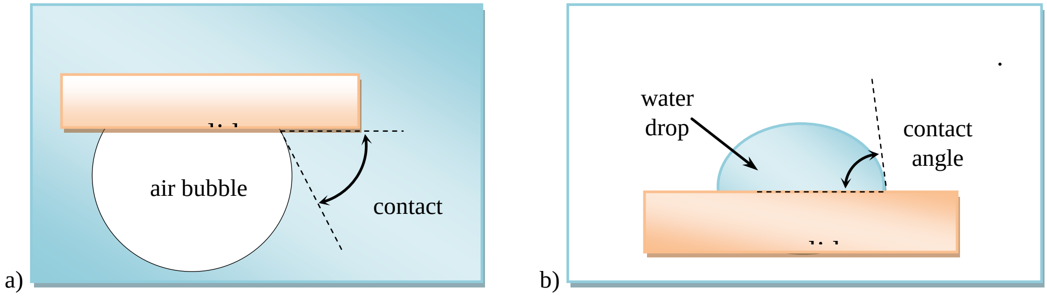


Fig. 1. The graphical representation contact angle θ measurements for captive bubble (a) and sessile drop (b) methods (after Drzymała, 2007)

2. EXPERIMENTAL

2.1. METHODOLOGY

The objective of this study was to determine the contact angle of as-is surface of copper-bearing shales using the captive bubble method. The contact angle was measured on the test stand composed of Surface Elektro Optyk device, model PHENIX 300 SEO (Phoenix, 2006) equipped with camera to take images of liquid drops or air bubble placed on outside surface of the sample and of ImageXP software used to analyse recorded image of air bubble. During the test, air bubble was brought using syringe with curved needle. The measurements using selected substances were carried out at least 10 times for all tested concentrations.

2.2. TESTED MATERIAL

A sample of copper-bearing shales taken from T240b heading in area of R-VIII shaft pillar of Rudna Copper Mine was used to measure the contact angle. Shale-type copper ore is difficult to concentrate and the most complex in terms of both, composition of waste rock and mineralization of useful ingredients. Permian shales (so called shale-type ore) form a series of interim formations from silty shales through dolomitic-silty and silty-dolomitic shales to the purely dolomitic ones. Mineralization of this ore is mainly of lenticular and vein stratiform. Dolomite in form of very fine grains forms thin streaks (Fig. 2) and silty material scattered among dolomite grains (Kijewski and Jarosz, 1996; Osika, 1983).

Fig. 2. Copper-bearing shale from T240b heading in area of R-VIII shaft pillar of Rudna Copper Mine (Poland)

2.3. REAGENTS USED

The contact angles of copper-bearing shales were measured using ethylene glycol butyl ether (C_4E_1), diethylene glycol butyl ether (C_4E_2) and dodecyphenol. For comparison purposes, the contact angle was also measured using captive bubble method in distilled water. All aqueous solutions of tested reagents were prepared using distilled water. The reagents used and their properties are specified in Table 1. Table 2 lists all tested concentrations of selected reagents. The tests were carried out in the same conditions and at constant temperature of 20 ^{o}C.

Table 1. The structures of the investigated reagents

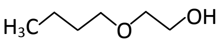
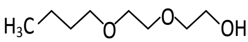
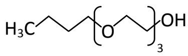
Properties	ethylene glycol butyl ether	diethylene glycol butyl ether	dodecyphenol
Structural formula			
Formula	$CH_3(CH_2)_3(OC_2H_4)OH$	$CH_3(CH_2)_3OC_2H_4OC_2H_4$ OH	$CH_3(CH_2)_3(OC_2H_4)$ $_3OH$
Molecular formula	$C_6H_{14}O_2$ (**C_4E_1**)	$C_8H_{18}O_3$ (**C_4E_2**)	$C_{18}H_{30}O$
Family	Polyglycols	Polyglycols	Alkohols
Purity	100%	≥ 99%	100%
Density	0.990 g/ml at 25 °C	0.953 g/ml at 20 °C	0.940 g/ml at 25 °C
Molecular weight (g/mol)	118.17	162.23	262.43
CAS number	9004-77-7	112-34-5	27193-86-8

Table 2. List of the tested reagents

Reagent	Purity %	Concentration mmol/dm^3	
Ethylene glycol butyl ether (C_4E_1)	100	1.06	16.92
		2.12	50,77
		8.46	
Diethylene glycol butyl ether (C_4E_2)	≥99	0.77	4.62
		1.54	6.16
		3.08	
Dodecyphenol	100	3,81	
		7,62	
		22,86	

3. MEASUREMENT RESULTS AND DISCUSSION

The contact angle of copper-bearing shales was measured using captive bubble method described above and selected reagents. Examples of images shown below (Fig. 2–5) were used to determine the contact angles. All averaged results obtained for each of investigated reagent concentration are given in Tables 3 through 5.

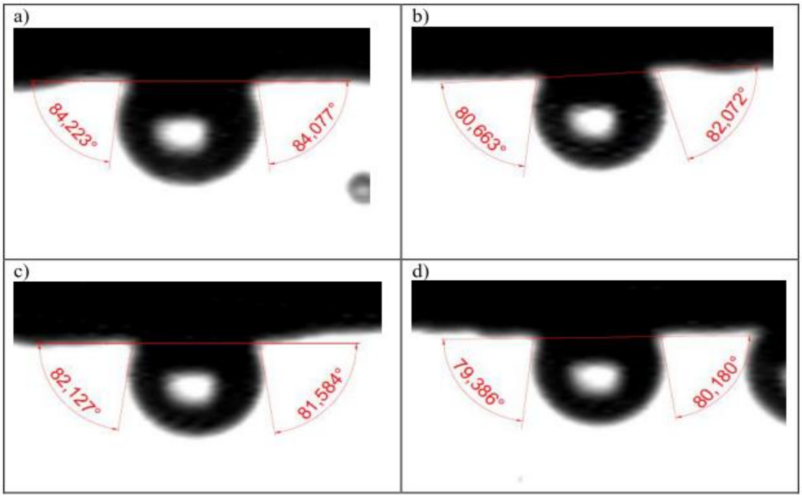


Fig. 2. Measurement of contact angle of copper-bearing shales immersed in distilled water using captive bubble method (a,b,c,d) (precision of the measurement results as shown by the program)

3.1. MEASUREMENT OF CONTACT ANGLE OF COPPER-BEARING SHALES IMMERSED IN DISTILLED WATER USING CAPTIVE BUBBLE METHOD

Fig. 2 shows examples of images taken during measurements of contact angle carried out using captive bubble method on as-is surface of a plate made of copper-bearing shales immersed in distilled water. The contact angles were marked and measured on obtained images using AutoCAD 2013 software.

The measured values of contact angles of copper-bearing shales immersed in distilled water were summarized and the average value of the angle was calculated. Analysis of contact angles showed their values fell within the range of 78°–84°, and the average value was of 82°.

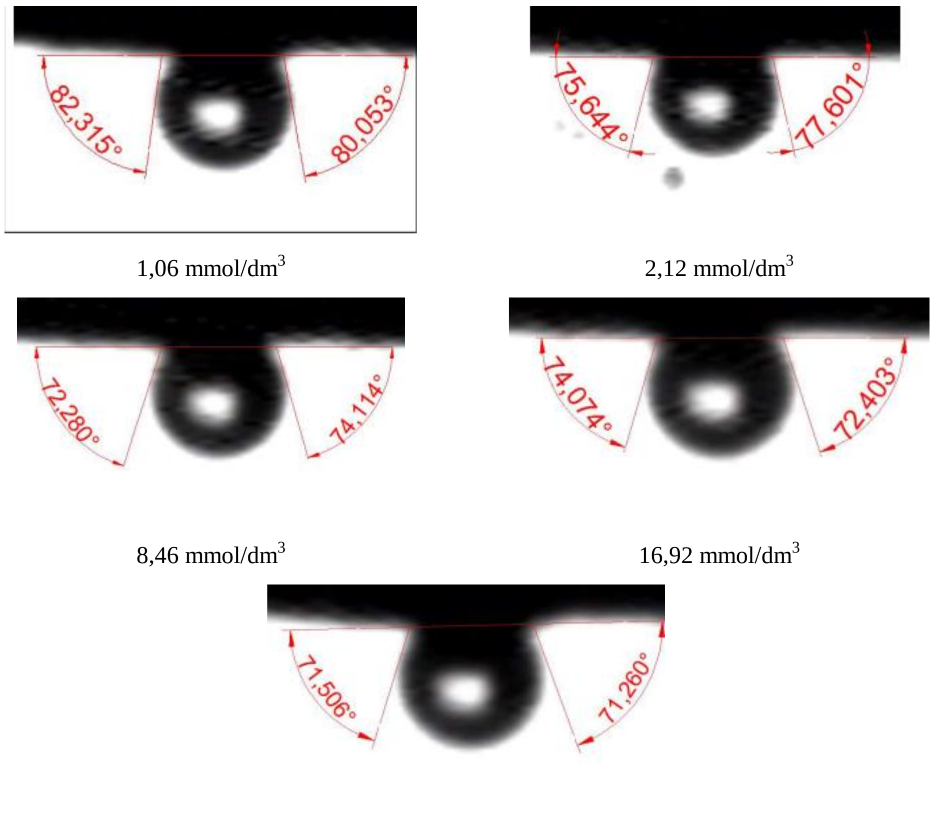


Fig. 3. Measurement of contact angle of copper-bearing shales immersed in aqueous solutions of ethylene glycol butyl ether (C_4E_1) using captive bubble method (precision of the measurement results as shown by the program)

3.2. MEASUREMENT OF CONTACT ANGLE OF COPPER-BEARING SHALES IMMERSED IN AQUEOUS SOLUTIONS OF ETHYLENE GLYCOL BUTYL ETHER (C_4E_1) USING CAPTIVE BUBBLE METHOD

Examples of images taken during the measurements of contact angle carried out using captive bubble method on as-is surface of a plate made of copper-bearing shales immersed in aqueous solutions of ethylene glycol butyl ether (C_4E_1) along with marked contact angles are shown in Fig. 3.

Table 3. Measured values of contact angle of copper-bearing shales immersed in aqueous solutions of ethylene glycol butyl ether (C_4E_1) using captive bubble method

Reagent	Concentration mmol/dm^3	Average value of contact angle in solution of a given concentration, θ	Average value of contact angle, θ
Ethylene glycol butyl ether (C_4E_1)	1,06	81	78
	2,12	81	
	8,46	78	
	16,92	78	
	50,77	74	

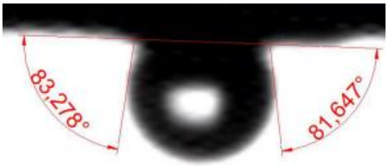
The average value of contact angle of copper-bearing shales immersed in aqueous solutions of ethylene glycol butyl ether (C_4E_1) amounts to 78° (Table 3).

3.3. MEASUREMENT OF CONTACT ANGLE OF COPPER-BEARING SHALES IMMERSED IN AQUEOUS SOLUTIONS OF DIETHYLENE GLYCOL BUTYL ETHER (C_4E_2) USING CAPTIVE BUBBLE METHOD

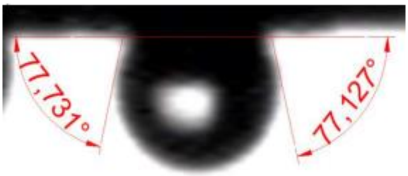
The contact angles were marked and measured on as-is surface of a plate made of copper-bearing shales immersed in aqueous solution of diethylene glycol butyl ether (C_4E_2) based on the images taken and using AutoCAD 2013 software (Fig. 4).

Table 4. Measured values of contact angle of copper-bearing shales immersed in aqueous solutions of diethylene glycol butyl ether (C_4E_2) using captive bubble method

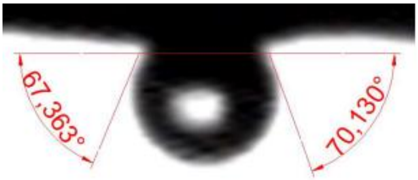
Reagent	Concentration mmol/dm^3	Average value of contact angle in solution of a given concentration, θ	Average value of contact angle, θ
Diethylene glycol butyl ether (C_4E_2)	0,77	81	76
	1,54	79	
	3,08	77	
	4,62	76	
	6,16	70	



0,77 mmol/dm^3 1,54 mmol/dm^3



3,08 mmol/dm^3 4,62 mmol/dm^3



6,16 mmol/dm^3

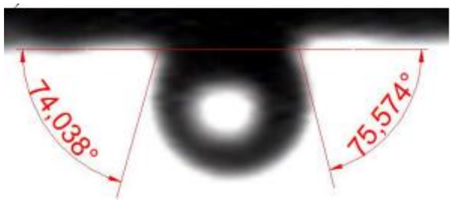
Fig. 4. Measurement of contact angle of copper-bearing shales immersed in aqueous solutions of diethylene glycol butyl ether (C_4E_2) using captive bubble method (precision of the measurement results as shown by the program)

The average value of the contact angle measured on as-is surface of copper-bearing shales calculated for all results obtained amounts to 81°. Individual measured values fall within the range from 70° to 81°.

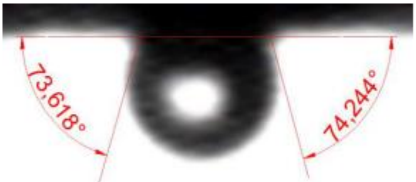
3.4. MEASUREMENT OF CONTACT ANGLE OF COPPER-BEARING SHALES IN AQUEOUS SOLUTIONS OF DODECYPHENOL USING CAPTIVE BUBBLE METHOD

When measuring the contact angles of copper-bearing shales in aqueous solutions of dodecyphenol using captive bubble method and Phoenix-300 measuring device, the images were taken and subsequently used to determine the values of the contact angles (Fig. 5).

3,81 mmol/dm^3



7,62 mmol/dm^3



22,86 mmol/dm^3

Fig. 5. Measurement of contact angle of copper-bearing shales in aqueous solutions of dodecyphenol using captive bubble method (precision of the measurement results as shown by the program)

The table below lists the values of the contact angles for the whole population of wetting results obtained in captive bubble method for copper-bearing shales immersed in aqueous solutions of dodecyphenol (Tab. 5).

Table 5. Measured values of contact angle of copper-bearing shales immersed in aqueous solutions of dodecyphenol using captive bubble method

Reagent	Concentration, mmol/dm^3	Average value of contact angle in solution of a given concentration, θ	Average value of contact angle, θ
Dodecyphenol	3,81	78	75
	7,62	75	
	22,86	73	

The analysis of the contact angles of copper-bearing shales immersed in aqueous solutions of dodecyphenol showed their values fell within the range of 73°–78°, and the average value was of 75°.

SUMMARY

This paper is aimed at determination of the contact angle of copper-bearing shales in the presence of various reagents and their various concentrations. The measured values of contact angle obtained for as-is surface of copper-bearing shales using captive bubble method are presented in Table 6. The tests were carried out on as-is surface of copper-bearing shales immersed in distilled water and in aqueous solutions of selected reagents (C_4E_1, C_4E_2 and dodecyphenol) of various concentrations.

Table 6. Measured values of contact angle of copper-bearing shales immersed in aqueous solutions of ethylene glycol butyl ether (C4E1), diethylene glycol butyl ether (C4E2) and dodecyphenol obtained using captive bubble method

Reagent	Concentration mmol/dm^3	Average value of contact angle in solution of a given concentration, θ	Average value of contact angle, θ
Distilled water	-	82	82
Ethylene glycol butyl ether (C_4E_1)	1,06	81	78
	2,12	81	
	8,46	78	
	16,92	78	
	50,77	74	
Diethylene glycol butyl ether (C_4E_2)	0,77	81	76
	1,54	79	
	3,08	77	
	4,62	76	
	6,16	70	
Dodecyphenol	3,81	78	75
	7,62	75	
	22,86	73	

Copper-bearing shales have natural slight hydrophobic properties. Nevertheless, in their study Drzymała and Bogosiński (1995) demonstrated that the copper-bearing shales do not undergo flotation in Hallimonda cell, which suggests they behave like hydrophillic substances during flotation process. To explain these contradictions, the attempt was made in this paper to interpret both phenomena.

Based on the measurements of the contact angle carried out it was observed that even the small concentrations of such reagents like C_4E_1, C_4E_2 and dodecyphenol caused a decrease in hydrophobicity of the surface of copper-bearing shales. However, frothers can facilitate the grain attachment to bubbles due to reduction a stability

of the thin film existing between the grain and the air bubble (Grodzka and Pomianowski, 2006; Aveyard and Clint, 1995). It gives a reason to assume that copper-bearing shales may only undergo flotation in the presence of frothers provided specific concentrations. This assumption is confirmed by the fact that the frothers play a very important role in flotation process. The frothers, in addition to formation of stable foam, acceleration of flotation rate and reduction of air bubble size, also modify the mineral grain hydrophobicity (Jańczuk et al. 2005).

CONCLUSION

The results obtained in the measurements of contact angle of copper-bearing shales coming from Legnicko-Głogwski Copper Mining Region using the captive bubble method on as-is shale surface demonstrate that the application of active surfactants causes the modification of natural shale hydrophobicity.

1. The measurements of contact angles showed that the addition of frothers such like C_4E_1, C_4E_2 and dodecyphenol decreases hydrophobic properties of copper-bearing shale surface.
2. The frothers investigated in this study probably reduce stability of thin film formed between the grain and air bubble.
3. The results of the tests of as-is copper-bearing shale surface suggest the shale flotation is possible in the presence of frothers, however proper selection of the frother concentrations is necessary to ensure effective flotation.

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