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EVALUATION OF LENGTH OF INTERACTION BETWEEN HYDROPHOBIC SURFACES FROM THE INDUCTION TIME MEASUREMENT

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An approach, reffered to here as the Scheludko-Malysa approximation has been used for the calculation of thickness of the rupturing film from the experimental values of air bubble – platinum, and air bubble – sulphide minerals, induction time (IT). The influence of applied potentials, pH, and flotation collectors on wettability is discussed. The results indicated a broad variation of IT. Calculated thickness of the rupturing film reaches some microns. It confirms a long-range character of the interactions between air bubbles and hydrophobic surfaces.

Key words: mineral flotation, hydrophobic interactions, rupturing film thickness

INTRODUCTION

Long-range attractive interaction between hydrophobic surfaces in water is well documented. Yoon (2000) clearly demonstrated how essential is to recognize the role of hydrophobic forces in flotation. A number of papers have been published that give a clear evidence that the electrostatic and van der Waals forces, neither of which are usually attractive (when both the bubbles and particles are charged negatively, that is the typical case in flotation practice), are not the only driving forces in a bubble-particle adhesion. All Derjaguin-Landau-Verwey-Overbeek (DLVO) forces (van der Waals and electrostatic forces) in the discussed systems are repulsive, but if the solid surface is hydrophobic, the wetting film ruptures, although there is no attractive interaction in the film. To find an explanation for this behaviour, a number of authors have postulated a "long-range hydrophobic force", but in the past years, it turned out increasingly that the reason for the rupture is the occurrence of nanoscaled gas bubbles adhering to the solid surface.

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The attachment of a solid particle to a gas bubble in flotation is the result of a complex process that is determined by hydrodynamic and surface effects and in an elementary flotation act it is possible to isolate the states before and after contact (Scheludko, 1967). For all types of proposed interactions the most important is how long and how strong they are.

Assuming that the thinning time of the liquid film between particle and bubble is equal to the induction time, an average thickness of the thin liquid film prior to its rupture at mineral surface could be calculated following the work of Malysa and his co-workers (Krasowska et al., 2003). To appreciate the impact of Scheludko and Malysa in the theoretical consideration of the problem and its implementation to IT experiments it will be called here the Scheludko-Malysa approximation. The Malysa-Scheludko approximation gives an opportunity to evaluate dependence of the critical distance for the rupture of the wetting film from the surface hydrophobicity.

In the present paper, experimental studies of wetting phenomena on platinum and sulphide minerals have been used. Thickness of the rupturing wetting films has been evaluated in the frame of the Malysa-Scheludko approximation by the air bubble induction time (IT) measurements. The paper contains studied electrochemical potential influence on IT. Results of the measurements of natural wettability and wettability induced by butyl-xanthate are reported. Also discussed potential dependence of the kinetics of dixanthogen layer formation on the surface of platinum and its influence on the thickness of the rupturing wetting films is presented.

EXPERIMENTAL

MINERALS

The minerals used in experiment were selected by hands. Their purity is shown in the Table 1.

Table 1. Sulphide minerals of IT experiments

Mineral	Formula	Principal mineral content, %	Mineral impurities
Pyrite	FeS_2	98-99	not determined
Chalcocite	Cu_2S	97-98	not determined
Chalcopyrite	$CuFeS_2$	94-97	pyrrhotite
Sphalerite	ZnS	95-96	galena, chalcopyrite
Molibdenite	MoS_2	99	not determined
Galena	PbS	99	not determined

For IT study, cylinders of minerals with diameters near 5 mm were mounted in a fluoroplast holder. The working surface was dry-polished in stages using alumina down to 0.05 μm and rinsed with distilled water or sometimes with ethanol between polishing stages.

IT EXPERIMENTS

IT was defined as the minimum time necessary for the attachment of an air bubble to the platinum surface. Experimental details of the procedure of the measurements of IT were described earlier (Vigdergauz and Nedosekina, 1998). Air bubbles for measurements were deposited on the holder from a small diameter flat-nosed needle positioned below the holder. The bubble formation and size were controlled using a combination of plug and needle. The movement of the bubble was observed through the wall of the cell, the latter being illuminated by an electric lamp. Figures 1 and 2 show the device, that was used for IT measurements under electrochemical polarization, and also bubble images, before and after attachment.

Fig. 1. IT measurements in conditions of electrochemical polarization:
1- the Glembotskii device for IT measurements; 2 - three electrode electrochemical cell;
3 - potentiostat PI-50-1.1.; 4 - programmer PR-8

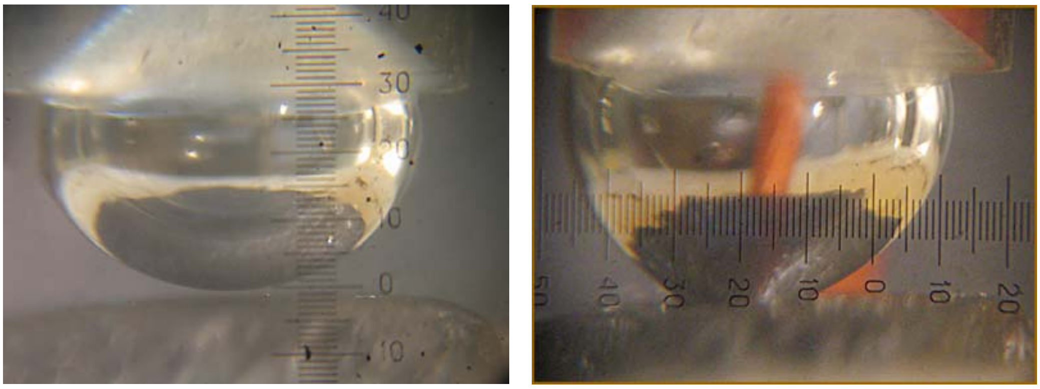

Fig. 2. The bubble before and after attachment during IT measurements

ELECTROCHEMICAL CELL

Electrochemical cell with a three-electrode system was used in potentially controlled IT experiments. Potentials were measured and were reported versus a silver-silver chloride reference electrode, which had a potential of +0.22V against the standard hydrogen electrode. The potential of mineral or platinum electrode was controlled by a potentiostat. A wire connected the working electrode to the external electrical circuit. The reference electrode was connected to the main compartment through a Lugging probe capillary. Current passed between the working platinum electrode and a platinum counter electrode, which was housed in the compartment, separated from the main cell by a sintered glass disc.

CALCULATION OF RUPTURING WETTING FILMS THICKNESS

For the evaluation of the thickness of the rupturing wetting films, the Malysa-Scheludko approximation (Krasowska et al., 2003). was used. According to Scheludko (1967), the thinning of the circular plane parallel film between a solid wall (non-slip conditions) and free surface (full mobility) can be described by the following relation:

$$\mathrm{d}(1/h^2)/\mathrm{d}t = 64\Delta P/3\eta a^2 \tag{1}$$

Where t is the time, η is the viscosity, a is the diameter of the film and ΔP is the difference between pressure inside the thin film and pressure in bulk phase.
After integration one obtains:

$$1/h^2 = 64(\Delta P/3\eta a^2)t \tag{2}$$

Taking into account that:

$$\Delta P = 2\gamma_{lv}/r, \tag{3}$$

where γ_{lv} is the surface tension for the liquid and r is the bubble radius, one can obtain that:

$$1/h^2 = 128(\gamma_{lv}/3\eta r a^2)t \tag{4}$$

For the case of experiment r_b = 1 mm, γ_{lv} = 72 mN/m, η = 0.001 Ns/m^2. The mentioned value for the surface tension of bubble-water interface has been used because no xanthate possesses a noticeable surface activity on the water-air interface. In comparison with the water-air value, γ_{lv} in 1 mM solutions of various xanthates does not decrease more than 2 mN/m (De Witt et al., 1935).

Calculations were done assuming constant average diameter of the baseline of the attached bubble a=0.7mm in the experiments. The reasons for such assumption was "rigid" form of the fixed on the holder bubble, that was used in the IT measurements (Drzymala and Vigdergauz, 2000). The calculations were performed under the assumption of the constant size of the thinning film. Symbol *a* denotes the diameter of the film (the average value in our experiments was 0.7mm) and this value was used in calculation as radius of the thinning film.

Obviously the obtained values of the critical length of the wetting film are very dependable on the base of the attached bubble that had been supposed to be critical for the rupture. Figure 3 illustrates *h*=f*(a)* dependence for stabilized other parameters of the experiment and IT values for 1s and 10 ms.

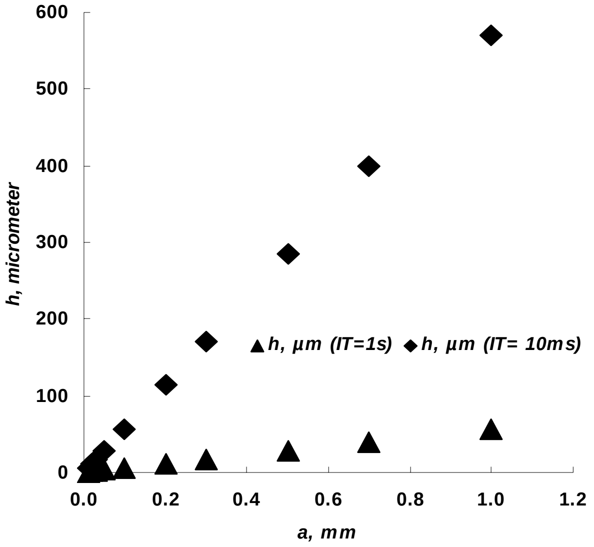

Fig. 3. Diameter of the rupturing film dependence of the critical thickness of the rupturing wetting film

A high-speed video sequence of the rupture of an aqueous wetting film on methylated glass shows that only one embryonic hole is sufficient to cause destabilization and dewetting of the entire film (Schulze et al., 2001). The mechanism of this rupture includes the presence of gas nuclei formed on heterogeneous surface sites.

Decrease of the IT values during repeated measurements (Drelich et al., 1997) and faster and easier flotation of the previously floated materials (Yoon, 2000) confirm in an indirect way the mechanism of strong long-range interactions as a result of the bubbles jump-in and jump-out. Possible transfer of reagents from bubble surface to the surface of mineral could not be the reason of the observed phenomena in the case of xanthate-induced hydrophobicity. Xanthate ions have little effect on the gas-solution interface (De Witt et al., 1935).

Attard (2005) mentioned that the force has been measured by AFM between surfaces separated by 0.3μm, which corresponds to about 1000 water molecules in width, and the idea that surfaces can induce order in liquids extending so far from the surfaces contradicts very fundamental theories of the liquid state.

Despite the limitations of the calculations by the Eq. 4 connected with parameter *a*, these limitations must not influence the evaluation of the trends and dependences of critical thickness of the rupturing film from pH, reagents consumptions and electrochemical polarization effects.

RESULTS AND DISCUSSION

PLATINUM ELECTRODE

Literature data on wettability of Pt-electrodes are controversial. Gardner and Woods (1974) had found that the surface of platinum electrode is hydrophilic. The reason was the observed contact angle that was below 10° at all potentials in the available region between hydrogen and oxygen evolution in 1M Na_2SO_4 and in 0.05M sodium tetraborate solution. This observation contradicts to the previous data of Gorodetskaya and Kabanov (1934) who found, that the surface of platinum was hydrophobic and angles up to 68° were shown.

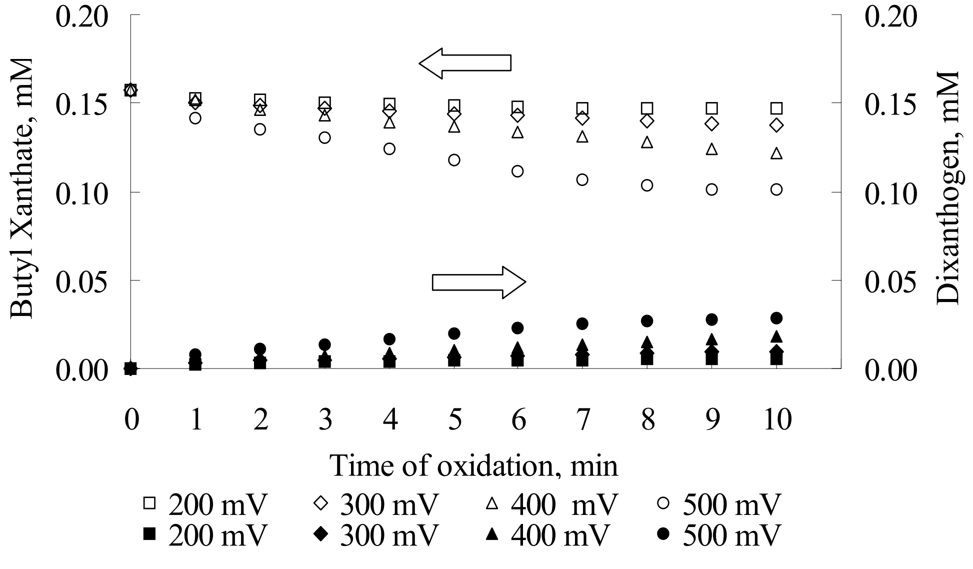

Fig. 4. Potential influence on the kinetics of xanthate electrochemical oxidation on platinum in neutral solutions: 1 – 150 mV; 2 – 200 mV; 3 – 300 mV

Cyclic voltammograms of Pt show that oxide formation begins near potentials of oxygen evolution and Pt surface is not oxidized in a wide area of potentials including potentials of the reported study (Chanturiya and Vigdergauz, 1993).

The study on xanthate oxidation and dixanthogen reduction kinetics shows the reversibility of the process. Figure 4 (Vigdergauz and Dorofeev, 2007) shows kinetics of xanthate oxidation and dixanthogen formation in neutral solution.

The study of the potential influence on the kinetics of xanthate oxidation on Pt shows its slowing down with increasing pH (Vigdergauz and Dorofeev, 2007). pH increasing slows down the formation of dixanthogen but its quantity is proportional to the charge in accordance with the Faraday law.

Table 2 summarizes results of the calculations of the thickness of the rupturing film based on the IT measurements in 20 mg/l xanthate solutions for various pH and potential values (Vigdergauz and Dorofeev, 2007).

Table 2. Time and potential of anodic polarization influence on the thickness of the rupturing film (nm) on Pt

pH 7.52 **pH 9.18**

E_{Pt}, mV	Time of oxidation, min				E_{Pt}, mV	Time of oxidation, min			
	1.5	4.5	7.5	10		1.5	4.5	7.5	10
150	215	230	250	400	150	200	200	215	215
200	215	250	600	400	200	200	215	230	230
300	215	400	800	900	300	215	230	250	280
400	400	730	800	900	400	230	250	280	400
600	400	900	1030	1250	600	280	400	600	600
700	400	900	1030	1250	700	330	600	600	680

pH 12.4

E_{Pt}, mV	Time of oxidation, min			
	1.5	4.5	7.5	10
150	NA*	NA	NA	NA
200	NA	NA	NA	NA
300	NA	NA	230	330
400	NA	250	330	400
600	280	280	330	400
700	280	400	400	400

NA* – no adhesion

Figure 5 shows dependence of the thickness of the rupturing film on the sorption density of dixanthogen which was produced by an electrooxidation at 700 mV for various pH values.

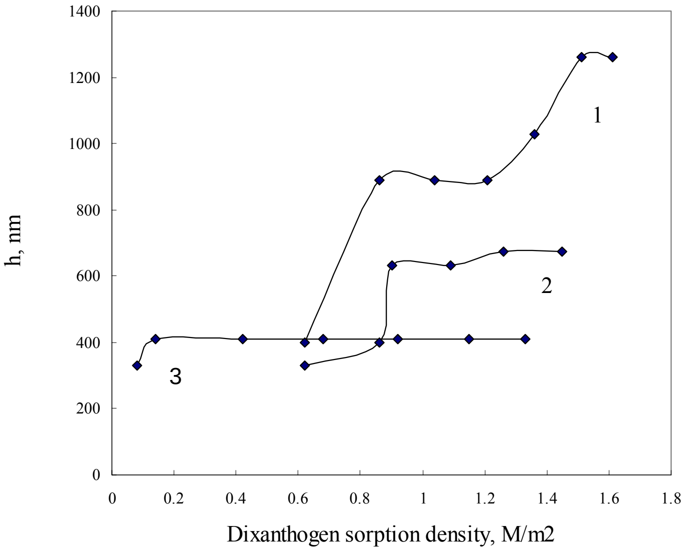

Fig. 5. pH influence on dependence of thickness of rupturing film and dixanthogen quantity on Pt produced by electrochemical polarization at 700 mV: 1 – pH 7.5; 2 – pH 9.2; 3 – pH 12.5

There is some "critical values" of sorption density, which initiate the fast adhesion. For neutral and weak alkaline solutions, these values of sorption density are near 0.9 M/m^2. Increasing pH leads to a slow down of adhesion and increases the critical thickness of the rupturing film due the hydrophilic hydroxyl-groups. The study of rupturing the wetting films on platinum indicates a broad variation of IT. The thickness of rupturing film that was calculated in the frame of the Malysa-Sheludko approximation reaches some microns and confirms a long-range character of the interactions between air bubble and hydrophobic platinum surface.

NATURAL WETTABILITY OF SULPHIDES

IT dependences on pH show hydrophilisation of sulphide minerals with increasing pH. Figure 6 (Vigdergauz et al., 2006) illustrates pH influence on the thickness of the rupturing film for sulphides without collector.

From the above results, it is seen that for more hydrophobic surfaces the film have been ruptured at longer distances. In the frame of the applied approximation under conditions of the experiment, average thicknesses of the thin liquid film prior to its rupture reaches 350 nm.

Calculations of the electrostatic repulsive forces show that they are negligibly small for such distances (Vigdergauz et al., 2006). The beginning of the rupture of the liquid film at such long distances shows the long-range character of the attractive forces. The nature of these forces is not quite clear until now, but in the past years it turned out increasingly that the reason for the rupture is most probably the occurrence of nanoscaled bubbles adhered to the solid surface (Stockelhuber et al., 2004; Ishida et al., 2000).

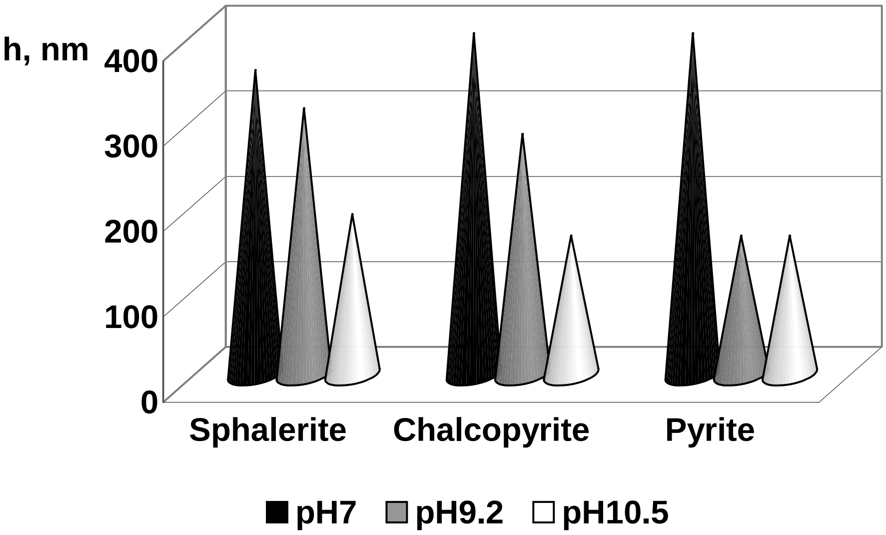

Fig. 6. pH dependence of the calculated thickness of rupturing film

Water structure changes near a hydrophobic surface facilitate formation of gaseous phase embryos. An approximate energy of the bubble-mineral interactions could be estimated basing on preposition that the detachment of an air bubble from the mineral surface is a reverse process to the bubble-mineral complex formation by jump-in of the nanobubbles on the solid hydrophobic surface with an air bubble. Detachment force values, after normalization to the contact area, give approximately an additional γ_{lv} that supplements 72 mN/m to the energy change (Vigdergauz, 2005).

XANTHATE INDUCED WETTABILITY OF SULPHIDES

Previous experimental study (Vigdergauz and Nedosekina, 1998) showed that increasing carbon chain length mainly resulted in decreasing IT. These data are in accordance with the well-known fact that an increasing length of alkyl chain of xanthate collectors stimulates flotation (Sutherland and Wark, 1955).

Figure 7 shows the calculated average thickness of the rupturing film on sulphides for various xanthates in borate buffer solution.

For studied sulphides, there is a observed tendency of an increasing average thickness of the rupturing film with increasing length of the hydrocarbon chain.

Table 3 (Vigdergauz, 2005) presents the dependence of IT on the potential of electrochemical polarization in borate buffer solution.

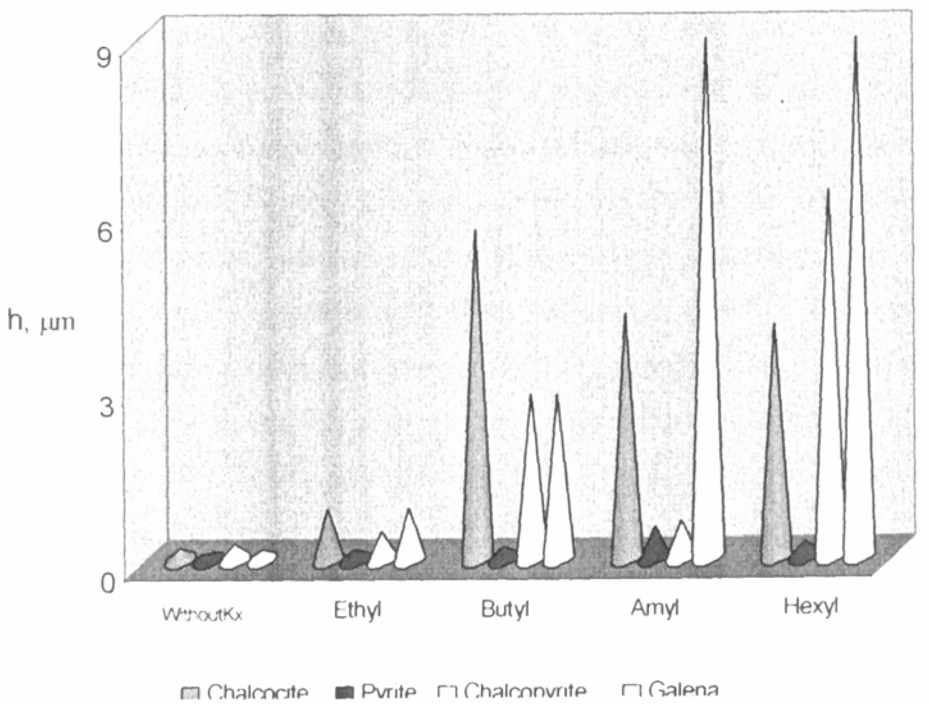

Fig. 7. Influence of carbon chain length of xanthate on the calculated thickness of the rupturing film

Table 3. Induction time for a gas bubble on sulphides at different potentials in 50 mg /dm^3 or 265μM amyl xanthate aqueous solutions

Applied potential [V]	Induction time [ms]			
	Chalcocite	Pyrite	Chalcopyrite	Galena
-0.8				4500
-0.6				3500
-0.4	3500			600
-0.2	3500	3500	4000	90
0	70	3000	2000	7
0.2	150	500	2000	2
0.4	200	4000	1500	25
0.6	2000		2000	
0.8	20		400	
1.0	3000		1500	
1.2	9		1500	

The obtained results (Table 3) indicate a broad variation of IT from 2 ms to 4.5 s.

Molibdenite is the most hydrophobic sulphide mineral and using the effect of hydrophobic interactions could be of special interest to improve molibdenite flotation. Lost of molibdenite during benefication of Cu-Mo ores remains one of the main problems of flotation practice. At Erdenet concentrator, for a 95% disintegration of mineral complexes, milling to 70% of the –74 µm fraction leads to increasing of the output of slimes. The design of the used scheme of milling and classification of Cu-Mo ores at the Erdenet plant gives output of the -5 µm fraction at the 10% level (Vigdergauz, 2005). The most prominent path for decreasing molibdenite losses with fine particles could be an implementation of selective flocculation technology that has been one of significant advances in mineral processing in recent years. An effect of a hydrophobic interaction of a hydrophobic polymer with the surface of naturally hydrophobic slimes was positively used for molibdenite flotation (Castro et al., 1997).

Figure 8 illustrates high hydrophobicity of molibdenite. Data calculated on the experiments of IT measurements in borate buffer solution for various potentials (Sohorov and Vigdergauz, 2007).

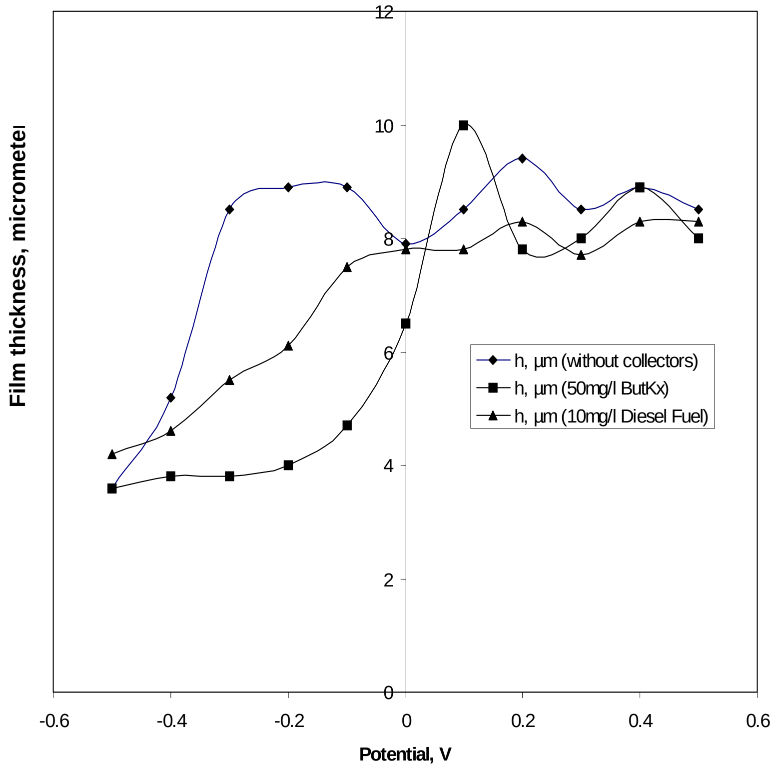

Fig. 8. Thickness of the rupturing film on molibdenite vs. potential of electrochemical polarization

Commonly used collectors, including diesel fuel or xanthate, do not increase hydrophobicity of this naturally highly hydrophobic mineral.

SUMMARY

Induction time measurements show that hydrophobic interactions are long-range. Calculated by the Sheludko-Malysa approximation values of the thickness of the rupturing films reach some hundreds of nanometers. The obtained values of the critical length of the wetting film are very dependable on the baseline of the attached bubble that had been supposed to be critical for the rupture.

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Użyto pewnej metody, w tej pracy nazwaną aproksymacją Scheludki i Malysy, do obliczenia grubości pękającego filmu. Oparto się na eksperymentalnych danych dotyczących czasu indukcji (IT) dla układu pęcherzyk powietrza – platyna oraz pęcherzyk powietrza - minerał siarczkowy. Przedyskutowano wpływ zastosowanego potencjału, pH i kolektora flotacyjnego na zwilżalność. Wyniki wskazują na duża zmienność IT. Obliczona grubość pękającego filmu wynosi kilka mikrometrów. Potwierdza to długo zasięgowy charakter oddziaływań pomiędzy pęcherzykami powietrza i hydrofobową powierzchnią.