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INFLUENCE OF FROTHER TYPE AND DOSE ON COLLECTORLESS FLOTATION OF COPPER-BEARING SHALE IN A FLOTATION COLUMN

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Abstract: In this paper the influence of nonionic (methyl isobutyl carbinol, tri(ethylene glycol) monobutyl ether) and cationic (hexylamine) frothers on flotation of copper-bearing shale in a flotation column was investigated. It was shown that naturally hydrophobic shale did not float in pure water but it floated in the presence of the investigated frothers. The real contact angle of shale, measured by the sessile drop method, was equal to about 40°, while its effective contact angle was zero when shale was floated in a flotation column in pure water. The investigated surfactants increased the effective hydrophobicity of shale from zero to 16±1, 22±1 and 33±2° for coarse, medium and fine particles, respectively. The calculations of the effective contact angle were based on a simplified probabilistic model of flotation.

Keywords: *flotation, hydrophobicity, frother, shale, flotation column*

Introduction

Froth flotation is a physicochemical process widely used in a mineral processing industry. Efficiency of flotation depends on such parameters as hydrophobicity of floating particles, properties of added chemical reagents, type of flotation devices and many others (Wills and Napier-Munn, 2006). Hydrophobic particles, having the contact angle greater than zero (Nguyen and Schulze, 2004), attach to gas bubbles, form stable particle-bubble aggregates, and move upwards to the froth layer, while hydrophilic particles sink.

The role of frothers in the recovery of solid particulate matter in froth flotation was studied by many authors (Heyes and Trahar, 1977; Malysa et al., 1987; Saleh and Iskra, 1996; Pugh, 2000; Laskowski, 2001; Drzymala et al., 2007; Farrokhpay, 2011; Kowalczuk et al., 2014). It is well known that frothers reduce bubble coalescence, stabilize bubbles in the froth layer (Cho and Laskowski, 2004) and shorten the time

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needed for formation of the three-phase contact (Kosior et al., 2011), leading to faster rupture of the liquid film between bubbles and solid particles. However, there is still a need to understand better the role of frothers in flotation, especially in collectorless flotation of solid materials under dynamic conditions. In this work we investigated the influence of non-ionic methyl isobutyl carbinol and tri(ethylene glycol) monobutyl ether as well as cationic hexylamine frothers on the maximum recovery, maximum size of floating particles, and effective hydrophobicity of naturally hydrophobic carbonaceous copper-bearing shale floated in a flotation column.

Experimental

The flotation experiments were carried out in a Plexiglas cylindrical flotation column having 0.82 m in height and 94 mm in diameter (Fig. 1). The column consisted of a collecting zone and a froth zone. The pulp was fed into the column near the top of the collecting zone. Starting from this point the solid particles were exposed to bubbles generated by an air sparger near the bottom of the column. The formed particle-bubble aggregates moved upwards to the froth zone and were collected as a concentrate, while the hydrophilic particles settled at the bottom of the column. The bottom part of the column was the collecting zone of non-floating particles.

A geological sample of carbonaceous copper-bearing shale originated from the Kupferschiefer stratiform copper ore mined by KGHM Polska Miedz S.A. The shale sample consisted of organic carbon, feldspar, silicates, dolomite and copper sulphide minerals. In the investigated sample the contents of Cu and total organic carbon were 7 and 8%, respectively. The density of shale was 2.5 g/dm^3, the isoelectric point of copper-bearing shale in water was pH=3.5 (Peng et al, 2014), while the point of zero charge measured by a titration method was pH=8 (Trochanowska and Kowalczuk, 2014).

The samples of carbonaceous copper-bearing shale were floated in the presence of two non-ionic (methyl isobutyl carbinol MIBC, tri(ethylene glycol) monobutyl ether C_4E_3) and one cationic (hexylamine) frothers (Table 1).

Table 1. Reagents used in flotation of investigated carbonaceous-copper bearing shale

Reagent	Molecular mass, g/mol
Methyl isobutyl carbinol (MIBC), $C_6H_{14}O$	102.2
Tri(ethylene glycol) monobutyl ether (C_4E_3), $C_4H_9O(C_2H_4O)_3H$	206.3
Hexylamine, $C_6H_{15}N$	101.2

A 6-gram sample of a narrow size fraction of shale was conditioned by stirring in a container for 5 min with either water (when floated without reagent) or aqueous solution of frother. The stirring speed was 350 rpm. Next, the mixture was pumped to the flotation column and subjected to flotation. The pumping time of the feed was 5 minutes and after this time only the aqueous solution of frother was pumped to the column. In each flotation tests the feed and aqueous solution flow rates were controlled by a peristaltic pump. The feed flow rate was 18 dm^3/h and the aqueous solution flow rate was 14 dm^3/h. The air flow rate was also controlled and kept constant at 116 dm^3/h. The floating particles were collected after 10, 30, 45 and 60 minutes of flotation as the froth products (concentrates). The non-floating particles, which assembled below the air sparger (Fig. 1) were collected after the end of flotation. The flotation products were dried at 105 °C and then weighted to determine the recovery of floating particles.

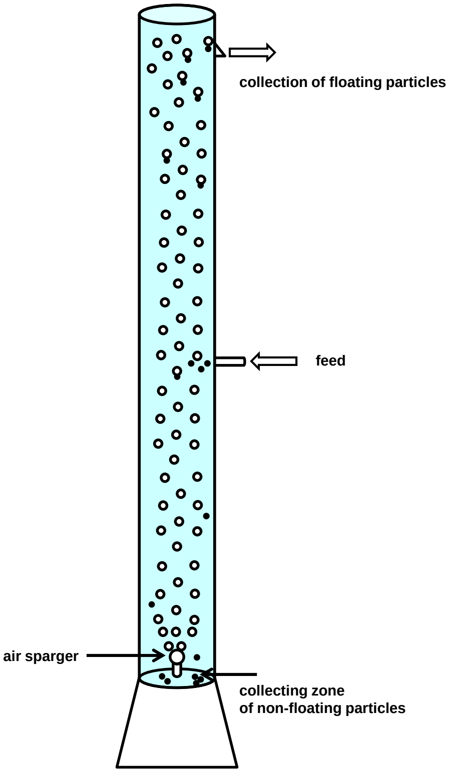
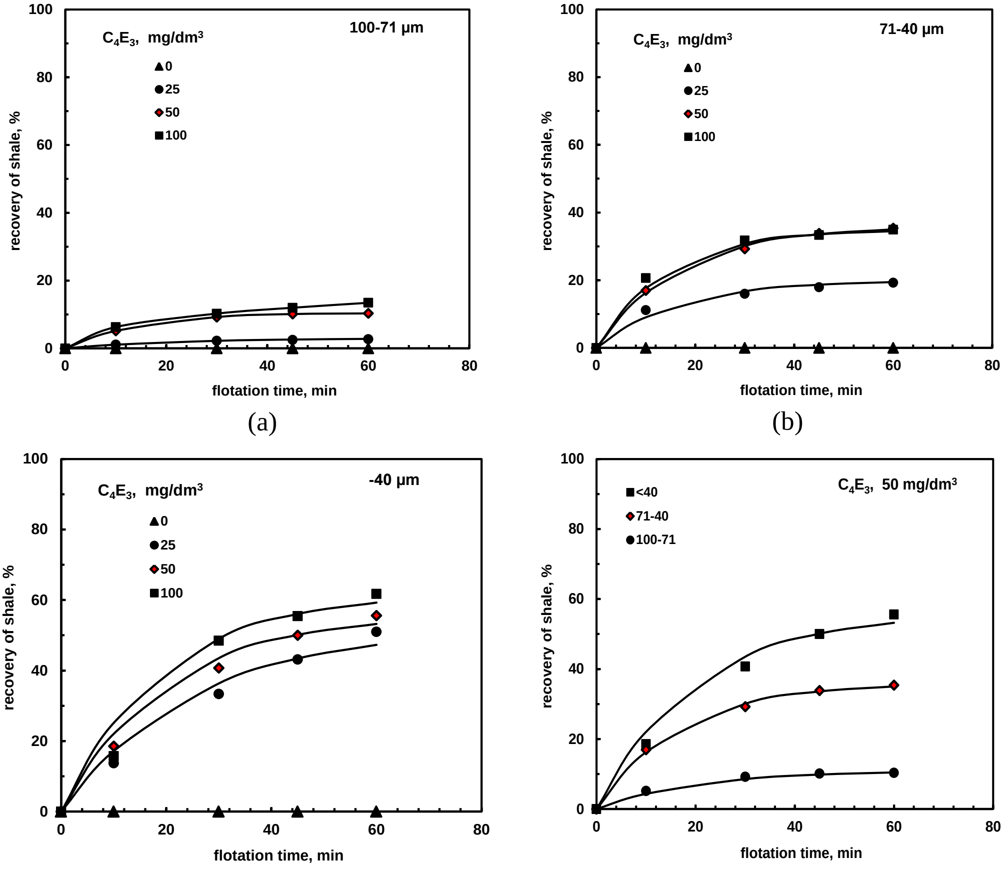


Figure 1. Scheme of flotation column used in experiments

Results and discussion

Flotation of carbonaceous copper-bearing shale was performed for three different particle sizes called coarse 100-71 µm, medium 71-40 µm and fine -40 µm fractions. Flotation was performed in pure water and in the presence of three different frothers, that is tri(ethylene glycol) monobutyl ether (C_4E_3), methyl isobutyl carbinol (MIBC) and hexylamine. When shale was floated in pure water, its recovery was zero for all particle size fractions (Fig. 2). A lack of flotation in pure water suggests hydrophilicity of the investigated shale sample. The same observation was made in our previous works (Drzymala and Bigosinski, 1995; Kowalczuk and Drzymala, 2011), in which flotation of shale was investigated in a Hallimond tube. There was no natural flotation of shale and its so-called flotometric contact angle in water was close to zero. On the other hand Bednarek and Kowalczuk (2014) showed that the advancing and receding contact angles of the investigated shale sample in water, measured by the sessile drop method, were 43 and 24º, respectively. It means that shale is a naturally hydrophobic material but its flotation in pure water is not possible, due to a stable water film between bubbles and particles. It appears that flotation of shale can be easily initiated and its sessile drop hydrophobicity "uncovered" simply by addition of frother to the flotation system.

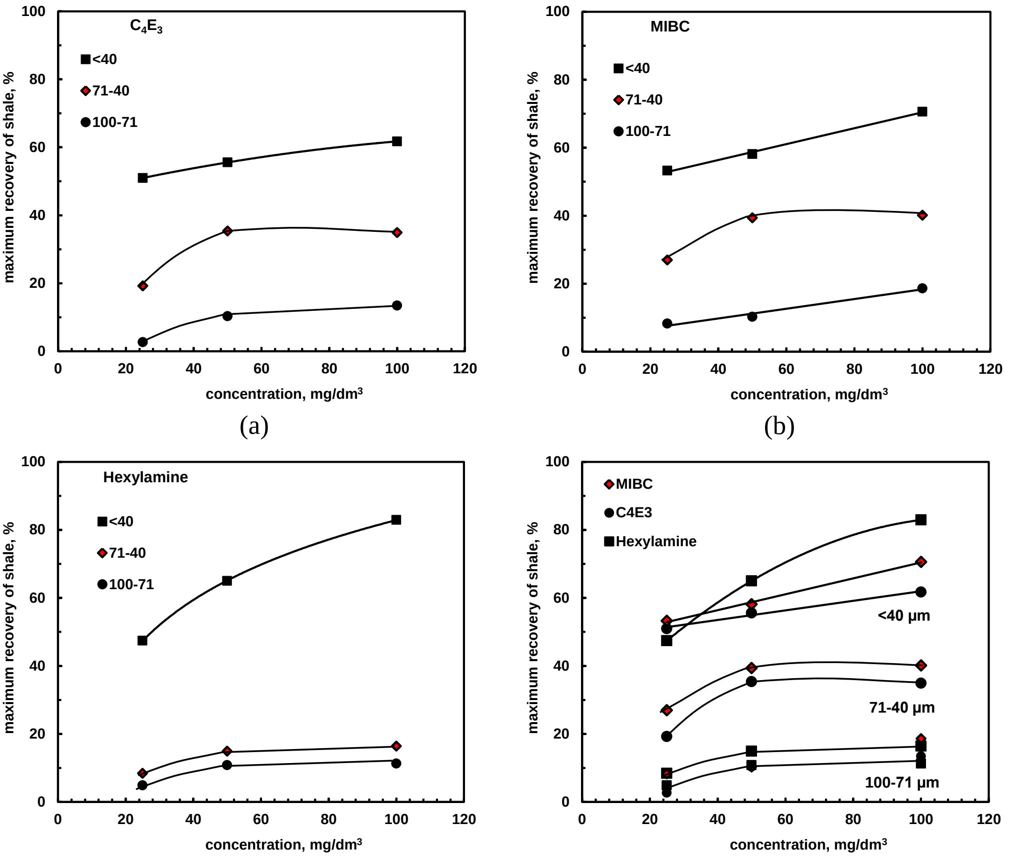


(a) (b)

(c) (d)

Fig. 2. Flotation kinetics of (a) coarse (100-71 μm), (b) medium (71-40 μm) and (c) fine (-40 μm) particles of carbonaceous copper-bearing shale in the presence of C_4E_3 (mg/dm^3) as well as (d) a comparison of flotation kinetics of shale in the presence of 50 mg/dm^3 of C_4E_3 for different shale size fractions

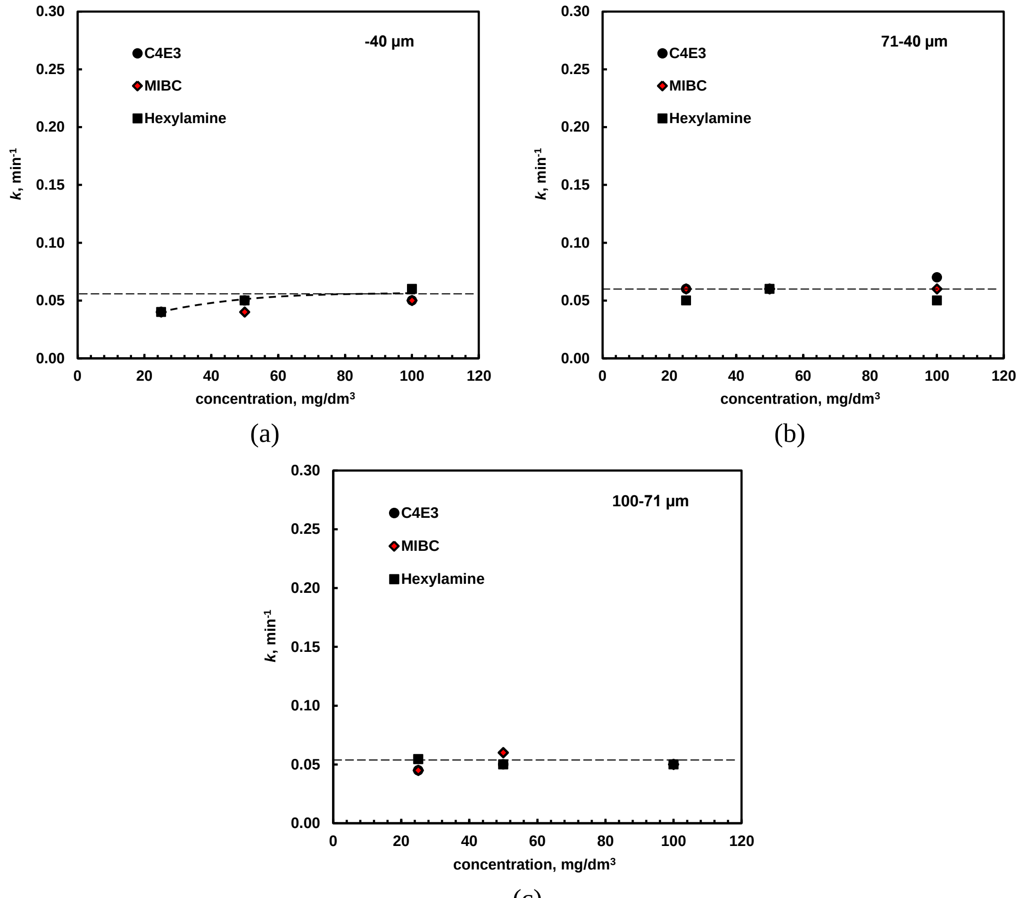
The results of flotation of investigated shale in the presence of frothers in the form of recovery of different particle size fractions and frother concentrations expressed in mg/dm^3 versus flotation time are presented in Figs. 2a-d. It can be seen that the recovery of coarse (Fig. 2a), medium (Fig. 2b) and fine (Fig. 2c) particle fractions increased with the frother concentration. The best results were obtained for the fine particles (Fig. 2d), while the lowest recovery was observed for the coarse particles in the presence of 25 mg/dm^3 of frother. The influence of frother concentration on the recovery of coarse, medium and fine samples was also observed for MIBC and hexylamine.



(a) (b)

(c) (d)

Fig. 3. Influence of frother type and dose on the maximum recovery of coarse (100-71 µm), medium (71-40 µm) and fine (-40 µm) particles; (a) C_4E_3, (b) MIBC, (c) hexylamine, (d) combined data taken from Figs. (a), (b) and (c)



(a)

(b)

(c)

Fig. 4. Influence of frother type and dose on flotation rate constant *k* of (a) fine (-40 µm), (b) medium (71-40 µm) and (c) coarse (100-71 µm) particles of copper-bearing shale

Figure 3 shows the influence of frother type and its concentration on the maximum recovery of coarse, medium and fine particles of carbonaceous copper-bearing shale floated in the flotation column. It can be seen from Figs. 3a-d that the maximum recovery of fine, medium and coarse particles increases with the frother dose. It was observed for all tested in this work frothers (Figs. 3a-d). The maximum recovery of coarse and medium particles reaches a certain plateau level at concentration of about 50 mg/dm^3. A further addition of frother does not change the maximum recovery of the coarse and medium particles. A high recovery of the fine particles is only possible at high frother concentrations. Figure 3d shows that the recovery-frother dose relationship can be divided into three regions: the first one for the coarse particles, where the recovery is very low (here lower than 20%); the second one, with recovery between 20 and 40%, for flotation of medium particles, and the third one, with the maximum recovery higher than 40%, for the fine particles.

While there is a strong influence of frother dose on the maximum recovery ($R_{\max}$) of coarse, medium and fine particles, Figs. 4a-c show that the frother type and concentration do not change the rate constant (k) of the first-order flotation kinetics for the medium (Fig. 4b) and coarse (Fig. 4c) particles. For carbonaceous copper-bearing shale, the 1st order rate constant k (s^{-1}) was calculated from the equation:

$$R = R_{\max}\left(1 - \mathrm{e}^{-kt}\right), \tag{1}$$

where t denotes flotation time. From Figs. 4a-c it can be seen that the values of k (min^{-1}) for the coarse and medium particles are almost the same but their maximum recoveries are different (Figs. 3a-d). Only for fine particles (Fig. 4a) the 1st order rate constant slightly increases with frother concentration. Most likely, this is due to a lower probability of the detachment of fine particles (Jameson, 2012). Muganda et al. (2011) showed that for coarse chalcopyrite particles having contact angles lower than 50° the first-order rate constant also changed only slightly.

Having flotation data for naturally hydrophobic shale it is possible to estimate the maximum size of flotation particles. The maximum size of floating particles $d_{\max}$ can be determined from the so-called separation curves of carbonaceous copper-bearing shale flotation data gathered in the presence of C_4E_3 (Fig. 5a), MIBC (Fig. 5b) and hexylamine (Fig. 5c). There are many definitions of $d_{\max}$. According to one of them $d_{\max}$ is the size of particles at which recovery is 50%. It is a good measure of $d_{\max}$ since, according to the theory of probability, at this point the particle has equal chance to either float or sink. Such $d_{\max}$ was previously used and discussed by Schulze (1977), Drzymala (1994), Chipfunhu et al. (2010) and Kowalczuk et al. (2011). The determined from Figs. 5a-c values of the maximum size of floating particles of shale ($d_{50}=d_{\max}$) as a function of frother concentration are given in Fig. 6. It can be seen that the values of maximum size of floating particles d_{50} depend on the frother type and concentration. Figure 6 shows that at low frother concentrations the d_{50} versus concentration curve is very steep, indicating that the higher frother concentration, the coarser particles can be floated. However, it has some limitation since at high frother concentrations the maximum size of floating particles remains almost constant, what can be clearly seen for C_4E_3 and hexylamine. For these frothers a further increase in concentration does not change the value of the maximum size of floating particles expressed as d_{50}. Only for MIBC it is possible to float coarser particles.

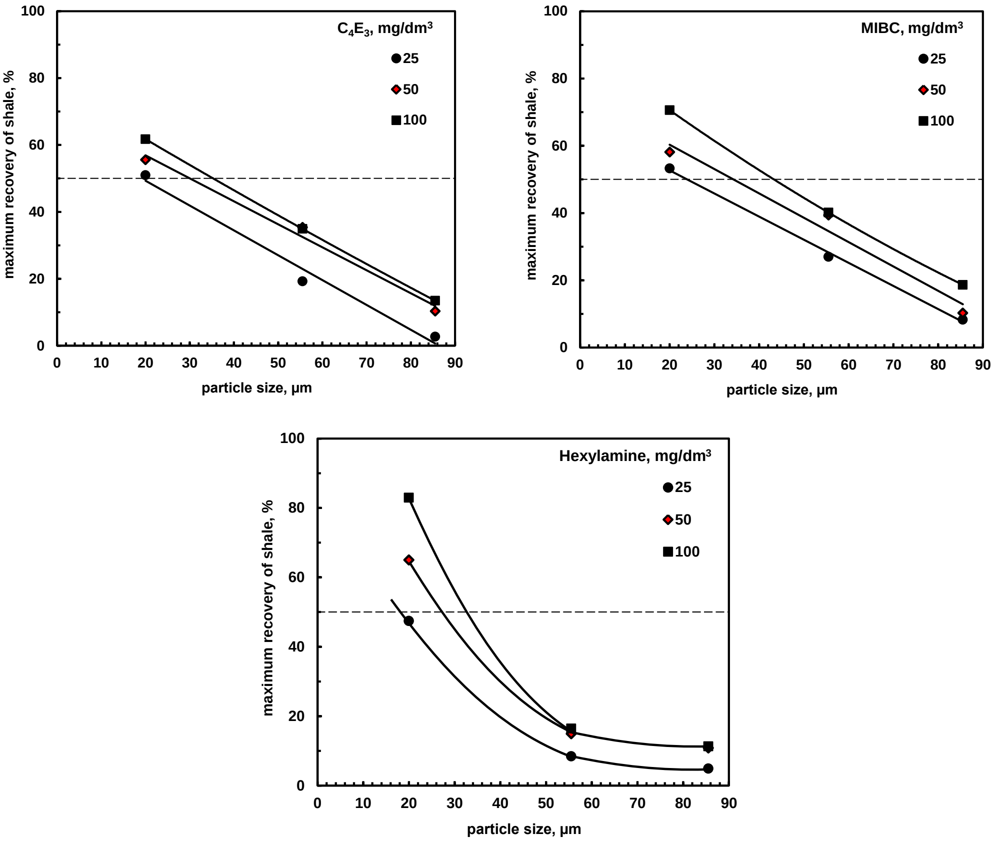


Fig. 5. Maximum recovery versus particle size of carbonaceous copper-bearing shale in the presence of (a) C_4E_3, (b) MIBC and (c) hexylamine expressed in mg/dm^3

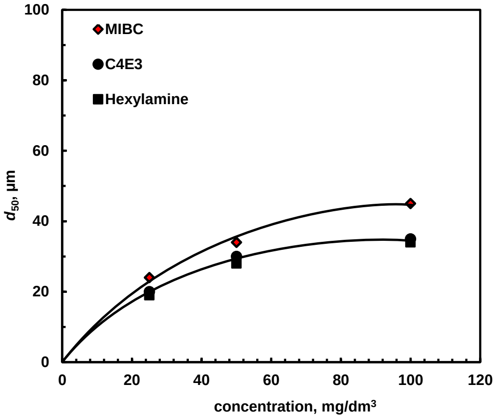


Fig. 6. Influence of frother type and dose on the maximum size of floating particles of copper-bearing shale

Presented in this work results clearly indicate that the non-ionic (MIBC, C_4E_3) and cationic (hexylamine) surfactants enhance the maximum recovery and maximum size of floating particles but do not change the kinetics of the process. It can be suggested that the mechanism of flotation is the same but for increasing frother concentration there is an increase in apparent hydrophobicity of shale evidenced by the increasing maximum recovery. However, as it has been discussed, the frothers do not change the real hydrophobicity of solid materials (Heyes and Trahar, 1977; Bednarek and Kowalczuk, 2014), but they change the effective hydrophobicity from zero up to the real, measured by the sessile drop method, hydrophobicity. To calculate the effective hydrophobicity of shale, which is "uncovered" by frothers, different methods, based on flotation theories (Scheludko et al., 1976; Varbanov et al., 1993; Drzymala, 1994; Watanabe et al., 2011), can be used to evaluate the effective contact angle of shale in the presence of the investigated frothers. One of them is the formula proposed by Varbanov et al. (1993), which is based on the probabilistic model of flotation and first-order kinetic equation:

$$\theta = \arccos\left(1 - k\frac{2\pi d_b^2 S}{3 d_p Q}\right), \tag{2}$$

where θ is the flotometric effective contact angle (°), k rate constant (1st order, s^{-1}), S the cross-section of a flotation cell (m^2), Q air flow rate (m^3/s), d_p particle size (m), d_b bubble size (m). For the used in this work column S= 0.007 m^2, Q=$3.2 \cdot 10^{-5}$ m^3/s, d_b=3.1 mm, d_p=20, 55.5 and 85.5 μm (mean of size fractions: 100-71, 71-40, -40 μm), while values of k are given in Figs. 4a-c.

Equation 2 permits to calculate the flotometric, that is effective, contact angle, whereas the rest (Young) contact angle can be calculated using the formula proposed by Scheludko et al. (1976) and Drzymala (1994):

$$\theta_r = \arcsin\left[\frac{d_p}{d_b}\sin(\theta/2)\right] + \theta/2\,. \tag{3}$$

The calculated values of the flotometric effective contact angle of different shale particle size fractions versus frother concentration are presented in Fig. 7. Since there was no flotation of shale in water, its effective contact angle was zero. It means that in pure water shale particles are hydrophilic (the flotometric contact angle is zero). An addition of frother initiated not only flotation of copper-bearing shale (Figs. 2-3) but also revealed its natural hydrophobicity (Fig. 7). Figure 7 shows that the effective hydrophobicity of shale does not depend on the frother type used in our investigations, including amine, which, when used with a short hydrocarbon chain (here 6 carbon atoms) works as a frother not as a collector (Ghigi, 1968). The calculated values of the maximum flotometric effective contact angles of coarse, medium and fine particles did not change with the frother dose and were 16±1, 22±1 and 33±2°, respectively. It shows that the maximum effective contact angle increases with decreasing particle size.

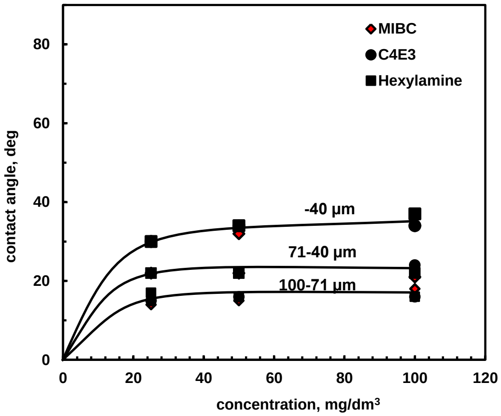


Fig. 7. Influence of frother type and dose on flotometric effective contact angle of coarse (100-71 µm), medium (71-40 µm) and fine (-41 µm) particles of copper-bearing shale

Conclusions

In this paper collectorless flotation of coarse (100-71 µm), medium (71-40 µm) and fine (-40 µm) particles of carbonaceous-copper bearing shale in the presence of non-ionic (MIBC, C_4E_3) and cationic (hexylamine) frothers was investigated. It was shown that naturally hydrophobic shale did not float in pure water. Flotation of shale was initiated by the presence of MIBC, C_4E_3 and hexylamine, which in the flotation process play the role of frothers. It was shown that the frother dose had a strong influence on the maximum recovery and maximum size of floating particles. The investigated in this work frothers enhanced flotation of shale by uncovering its natural hydrophobicity, observed by the sessile drop measurements, and being equal to about 40°. The effective hydrophobicity of the investigated shale was dependent on the frother dose, while the maximum effective hydrophobicity was only dependent on the particle size.

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