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Flotation, surfactants
Critical Coalescence Concentration (CCC)

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CRITICAL COALESCENCE CONCETRATION (CCC) AS A PARAMETER FOR EVALUATION OF SELECTED QUATERNARY AMMONIUM COMPOUNDS

The objective of this paper was to determine the Critical Coalescence Concentration (CCC) of surfactants such as N(dodecyloxycarboxymethyl) N,N,N-(trimethylammonium) bromide (DMGM-12), N-[2-(dodecyoxycarboxy)ethyl] N,N,N-(trimethylammonium) bromide (DMALM-12) and N-[3-(dodecanoyloxycarboxy)prophyl] N,N,N-(trimethylammonium) bromide (DMPM-11). The surfactants used represent quaternary ammonium compounds containing a hydrophobic moiety with an ester group (commonly known as “esterquats”). The CCC value was determined by analysis of the relationship between concentration of surfactant and average air bubble diameter. The values of the critical coalescence concentration (CCC) were estimated using a graphical method.

1. INTRODUCTION

Floatation is the one of enrichment processes which is commonly used in mineral processing technology. One of the important factor influencing flotation is the property of the reagent, which is introduced to flotation suspension. The reagents modify hydrophobicity, and thus, flotation both naturally hydrophobic and hydrophilic materials. The chemical compounds used in flotation process can be classified into four groups: collectors, modifiers (frothers, activators, and depressors), hydrophobization agents and electrolytes. Each of these groups influences flotation process in a different

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manner. Collectors and frothers (frequently called „foaming agents") play the most important role in the flotation process.

Flotation collectors cause hydrophobization of hydrophilic or slightly hydrophobic particles present in the floatation pulps. Selective hydrophobization is the they for action for separation of particles of various solids by flotation. Selectivity of the collection results from differences in adsorption occurring on certain solid particles in the flotation suspension. Flotation collectors modify not only hydrophobic properties of articles but also influence the contact time of a particle with gas bubbles, froth formation and froth stability.

Frothers are used to disperse gas, produce stable froth, and accelerate flotation process (Drzymała, 2007). Introduction of a frother to the solution causes reduction of air bubble size (Fig. 1). The bubble size drops owing to the reduction of solution surface tension. Figure 1 shows bubble size of methyl isobutyl carbinol (MIBC) vs. frother concentration. In the case when the bubbles are mechanically produced, the change of their size occurs at much lower concentrations (Drzymała, 2007).

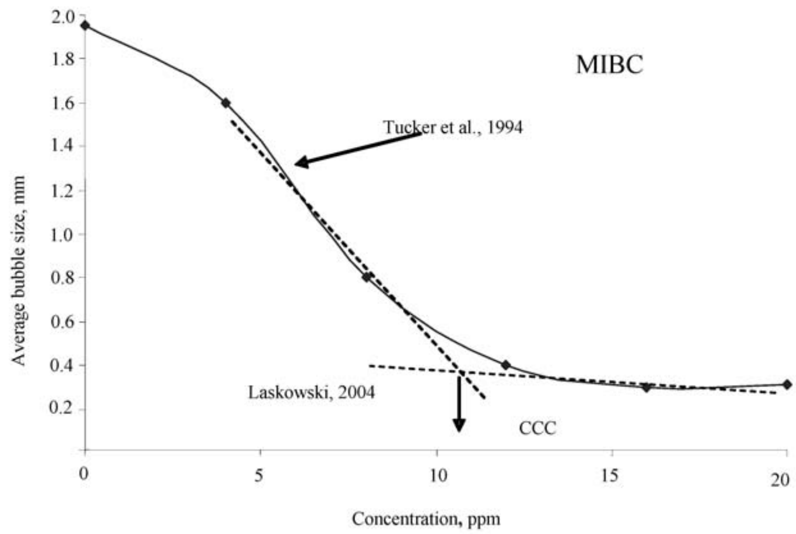


Fig. 1. Influence of concentration frother on properties of the gas-water system for methyl isobuthyl carbinol (MIBC) and CCC determination (Laskowski, 2004; Tucker et al.,1994; Drzymała, 2007)

Various parameters are used to describe the frothers. Among them, the so called "Critical Coalescence Concentration" (CCC) seems to be the most useful. This parameter was introduced in 2002 by Laskowski (2002a,b). The CCC is a minimum frother concentration, at which the coalescence, in a reasonable period of time, is completely prevented. It can be determined by a graphical method proposed by Laskowski (2002) (Fig. 1).

The shape of the average bubble size vs. frother concentration is similar for many surfactant as it is shown in Figures 2–3.

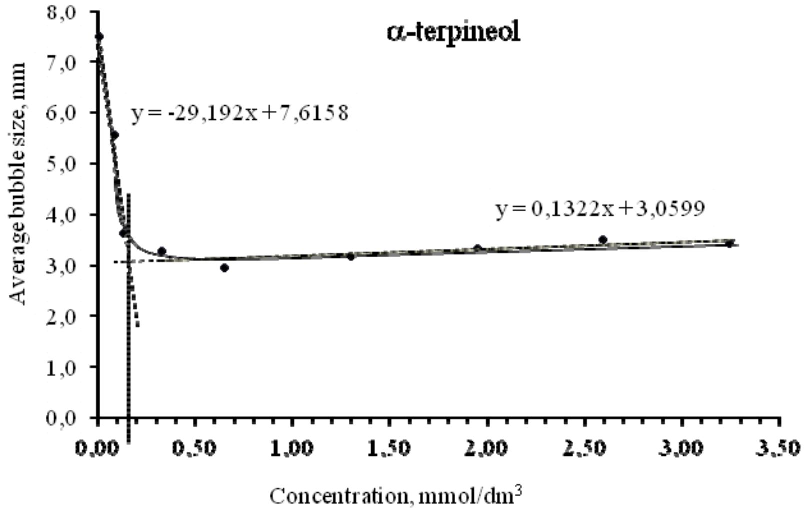


Fig. 2. Critical coalescence concentration (CCC) for α-terpineol (Szyszka et al., 2006)

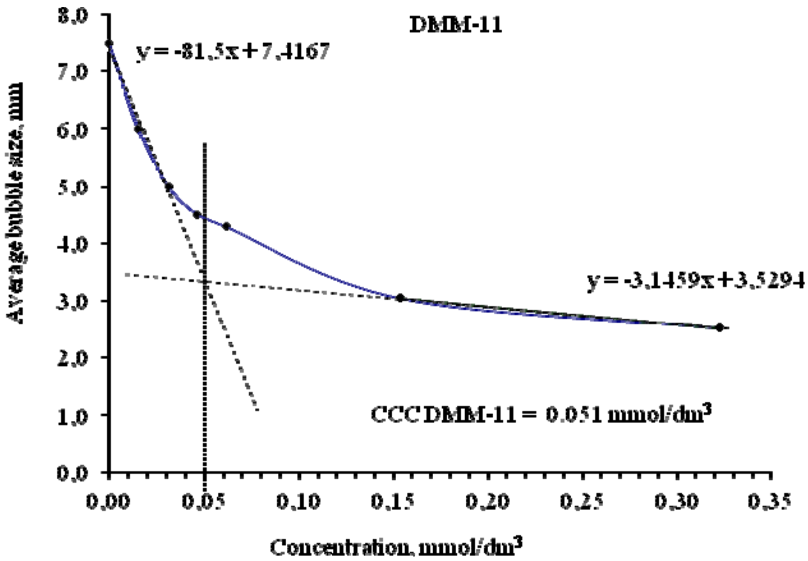


Fig. 3. Critical coalescence concentration (CCC) for DMM-11 (Szyszka et al., 2006)

Frothers adsorbed at air the bubble surface form thin and rough films. Therefore, if the solution does not contain any frother, water may freely flow between air bubbles and the bubbles undergo quick coalescence (Drzymała, 2007).

The reagents used in this paper are degradable quaternary ammonium salts, which are widely used in pharmaceutical, cosmetic and paper industry as well as in agriculture. Some authors (Koeppl et al., 1997) report that the quaternary ammonium salts have been also used as collectors in flotation of sulfide-free ores. In this paper the question was asked whether the quaternary ammonium salts have good foaming properties and ability to reduce surface tension of solutions and may be used as frothers. The objective of this paper was to test the selected bio-degradable surfactants and check the possibility to use them as flotation frothers by determination of their critical coalescence concentrations (CCC). The conducted tests were of cognitive nature and at the same time they provided information necessary to determine whether the critical coalescence concentration might be a sufficient criterion to evaluate the possibility of using them as frother in flotation.

EXPERIMENTAL

1.1MATERIALS AND CHARACTERIZATION

N(dodecyloxycarboxymethyl) N,N,N-(trimethylammonium) bromide (denoted as DMGM-12), N-[2-(dodecyoxycarboxy)ethyl] N,N,N-(trimethylammonium) bromide (denoted as DMALM-12) and N-[3-(dodecanoyloxy)prophyl] N,N,N-(trimethylammonium) bromide (denoted as DMPM-11) were used in the tests. Their formula, molecular weight and solubility are given in Table 1.

Table 1. Surfactants used in tests

Chemical formula	Structural formula	Molecular weight g/M	Solubility
DMGM-12 $C_{17}H_{36}O_2BrN$	$(H_3C)_2(CH_3)N^{\oplus}-CH_2COOC_{12}H_{25}\ Br^{\ominus}$	366.0	no limited
DMALM-12 $C_{18}H_{38}O_2BrN$	$(H_3C)_2(CH_3)N^{\oplus}-CH(CH_3)COOC_{12}H_{25}\ Br^{\ominus}$	368.0	no limited
DMPM-11 $C_{18}H_{38}O2BrN$	$(H_3C)_2(CH_3)N^{\oplus}-CH_2CH_2CH_2OCOC_{11}H_{23}\ Br^{\ominus}$	368.0	no limited

The tested surfactants were synthesized in the laboratory of the Chemical Faculty of Wroclaw University of Technology (Luczyński, 2000). The solutions for testing were prepared using distilled water and the original solutions held.

2.2. METHODS

The sizes of air bubbles were measured in an apparatus made in the laboratory of Mineral and Waste Processing of Wrocław University of Technology (Szyszka, 2006). It consisted of peristaltic pump (1) producing air bubbles, pressure equalization tank (2), compressed air supply conduits and flotation cell (3) (Fig. 4). The flotation cell was provided with a retainer to hold capillaries producing air bubbles. Rubber hoses were used to supply compressed air from the peristaltic pump to capillaries. The formed air bubbles were recorded by a NIKON Coolpix 5700 digital camera (4) (Fig.4).

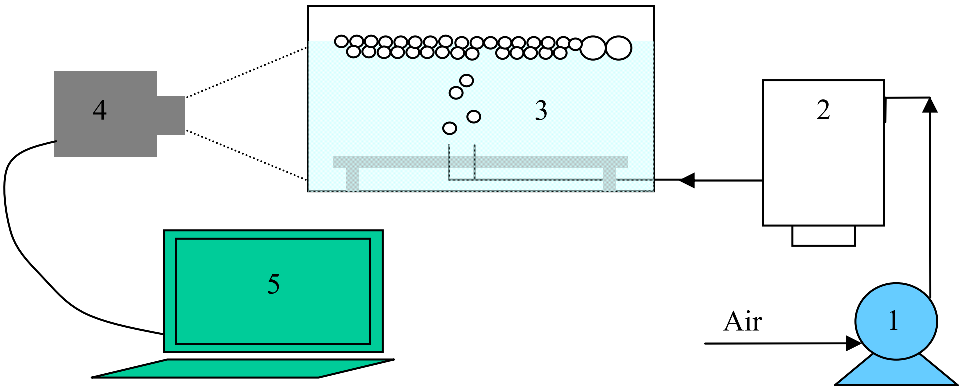


Fig. 4. Experimental set up for CCC measurements:
1) peristaltic pomp, 2) equalizing tank, 3) cell, 4) digital camera, 5) computer (Szyszka, 2006)

The desired concentrations of the tested frothers were achieved by dilution of the original solution. The concentration of the original solution was 0.1% (w/w). All tested frother solutions were prepared in the same way using distilled water.

The digital photo camera, which was used to take series of photos for each tested solution was located at a fixed distance from the flotation cell of volumetric capacity of 89 cm^3 (Fig. 4). The photos were subsequently assessed by a graphics software Corel PhotoPaint 12. Only diameters of clearly visible air bubbles present at the solution surface were measured. Next, the average diameter of air bubbles for each tested concentration of surfactant solution was determined. The same measurement method was used to all tested surfactants. The graphs showing a relationship between the average value of air bubble diameter and concentration of tested solution were plotted and subsequently the CCC values were determined using the graphical method described by Laskowski (2002 a,b). The critical coalescence concentration (CCC) was determined using a linear regression method. The CCC it is the point of intersection of straight lines approximating the decreasing average size of air bubbles and the increasing frother concentration, projected down to the X axis. The average diameter of the air bubbles was calculated as an arithmetic mean and also by using the following formula:

$$d_{srS} = \frac{\sum d^3}{\sum d^2} ,$$

called the Sauter mean diameter (Pacek et. al., 1998).

2.3. RESULTS AND DISCUSSIONS

2.3.1. MEASUREMENTS OF AVERAGE DIAMETER OF AIR BUBBLE FOR DISTILLED WATER

In previous papers (Szyszka, 2006, 2008) average diameter of air bubbles in distilled water without any addition of frothers using the same measuring apparatus was measured. Irregular air bubbles easily undergo coalescence in distilled water and the Sauter diameters of bubbles was 6.94 mm.

2.3.2. DETERMINATION OF CCC VALUE FOR DMGM-12

First series of measurements were conducted for the DMGM-12 surfactant. The average air bubble diameter was determined basing on the bubbles photographs. In order to obtain the measured values as accurate as possible, only photographs from which at least 50% of bubbles size could be measured were considered for evaluation. The results are given in Table 2.

Table 2. Average diameters of air bubbles for tested concentrations of DMGM–12 frother

DMGM-12									
Concentration, % wt	0.5	0.1	0.075	0.05	0.0015	0.0012	0.0010	0.0005	0.0002
Concentration mmol/dm^3	13.59	2.72	2.04	1.36	0.04	0.03	0.03	0.014	0.005
Average bubble size mm	1.16	1.51	1.73	2.23	2.83	2.85	3.26	3.37	4.10
Average bubble size Souter, mm	1.16	1.51	1.73	2.24	2.87	2.96	3.28	3.38	4.13

The graph relating the average diameter size of air bubble and concentration of analyzed solution was plotted basing on the measured values and shown in Fig. 5. As a result of graphical analysis of the measured parameters values, the critical coalescence concentration (CCC) of the tested surfactant was determined. Its value (arithmetic mean) was 0.041 mmol/dm^3.

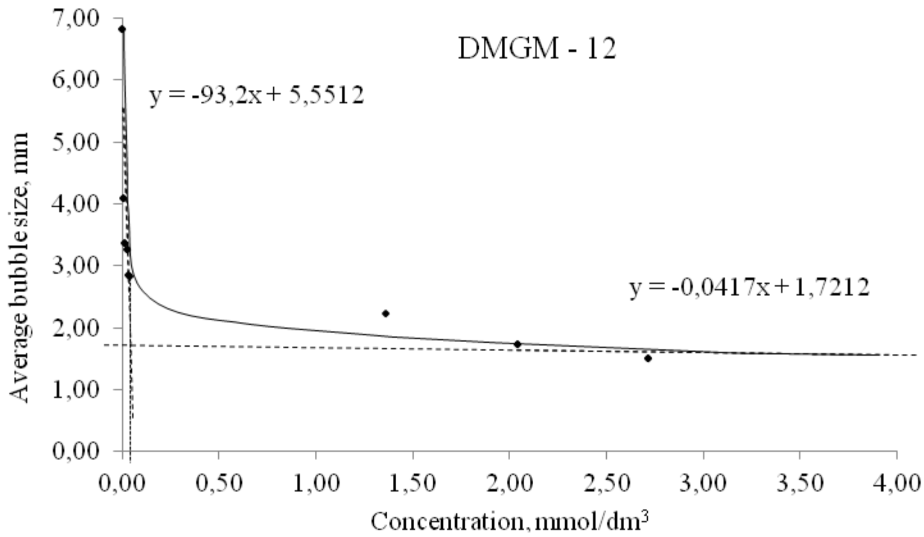


Fig. 5. Critical coalescence concentration (CCC) for DMGM-12

As shown in Fig. 6, the Sauter mean diameter of air bubbles vs. concentration of tested surfactant solution provided values equal to 0.042 mmol/ dm^3.

No considerable variation of CCC determined with use of arithmetic and Sauter mean values of air bubble diameter was observed for the tested DMGM-12 surfactant.

2.3.3. DETERMINATION OF CCC VALUE FOR DMALM-12

The tests of another surfactant, DMALM-12, were carried out in the same manner as described above. The average air bubble diameter was also determined basing on bubbles photographs. In order to obtain the measured values as accurate as possible, only the photographs on which at least 50% of air bubbles could be measured were considered. The average diameters of air bubbles for tested concentrations of DMALM-12, based on photographs, was measured. The measurement results are given in Table 3.

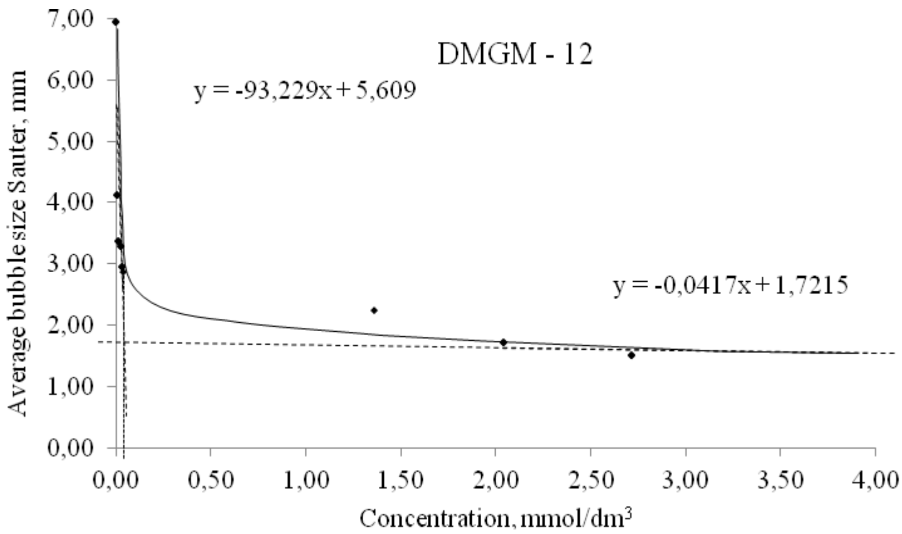


Fig. 6. Critical coalescence concentration (CCC) for DMGM-12

Based on the photos taken, the diameters of air bubbles for individual surfactant concentrations were measured. The measurement results are given in Table 4.

Table. 3. Average diameters of air bubbles for tested concentrations of DMALM-12

DMALM-12									
Concentration, % wt	0.1000	0.0750	0.0500	0.0015	0.0012	0.0010	0.0005	0.0002	woda
Concentration, mmol/dm^3	2.72	2.04	1.36	0.04	0.03	0.03	0.01	0.01	0.00
Average bubble size, mm	1.50	1.57	1.50	2.54	2.65	2.64	2.82	4.25	6.83
Average bubble size Souter, mm	1.50	1.58	1.51	2.58	2.58	2.61	2.92	5.08	6.94

Coalescence of DMALM is shown in Figs 7 and 8.

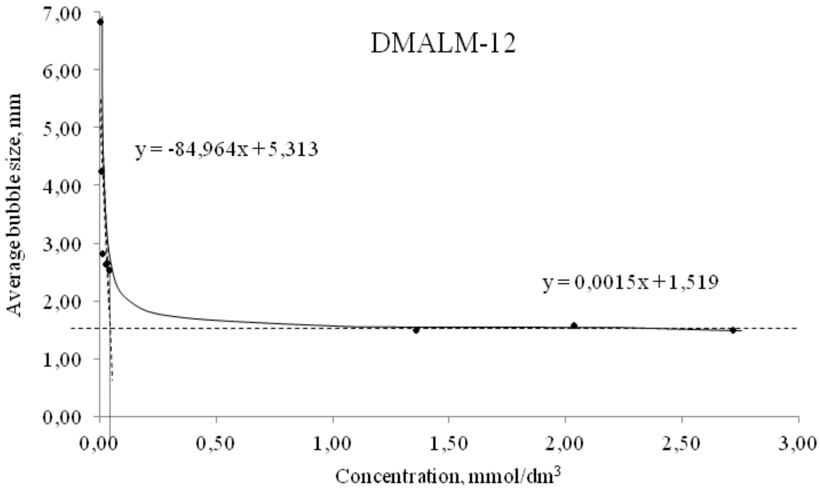


Fig. 7. Critical coalescence concentration (CCC) of DMALM-12

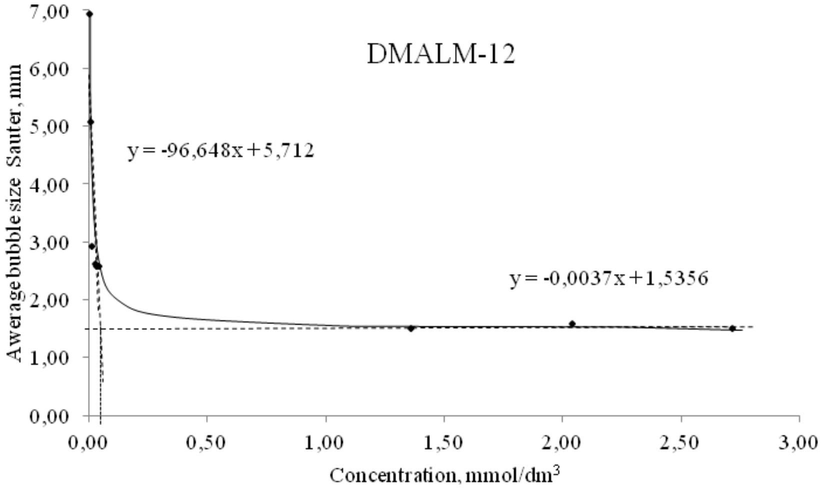


Fig. 8. Critical coalescence concentration (CCC) for DMALM-12

The measured values were used to plot a relationship between the concentration of DMALM-12 surfactant and the arithmetic mean of air bubble size (Fig. 7). The same method of graphical interpretation was used to determine the CCC value of the DMALM-12 surfactant. Basing on the curve, the critical coalescence concentration of the tested surfactant was determined. The CCC value for the DMALM-12 surfactant is equal to 0.045 mol/dm^3 when the average bubble size is calculated as on arithmetic mean, while for the Sauter mean the CCC is 0.043 mmol/dm^3 (Fig. 8).

Also in this case, like in the case of DMGM-12, the CCC values of DMALM-12 determined with use of both average diameter concepts are comparable.

2.3.4. DETERMINATION OF CCC VALUES OF DMPM-11

The third tested surfactant was DMPM-11. The average diameter of air bubbles for this surfactant was also determined on the basis of selected photographs. The calculated values of air bubble diameters are specified in Table 4.

The results obtained were used to plot the graphs of the relationship between the concentration of DMPM-11 frother and the arithmetic mean value (Fig. 9) and Sauter mean value (Fig. 10) The CCC values of the tested surfactant were read from the graphs and amounted to 0.048 mmol/dm^3 and 0.047 mmol/dm^3, respectively.

Table. 4. Average diameters of air bubbles for tested concentrations of DMPM-11

DMPM-11									
Concentration, % wt.	0.1000	0.0750	0.0500	0.0015	0.0012	0.0010	0.0005	0.0002	woda
Concentration mmol/dm^3	2,72	2,04	1,36	0,04	0,03	0,03	0,01	0,01	0,00
Average bubble size mm	1,50	1,57	1,50	2,54	2,65	2,64	2,82	4,25	6,83
Average bubble size Souter, mm	1,50	1,58	1,51	2,58	2,58	2,61	2,92	5,08	6,94

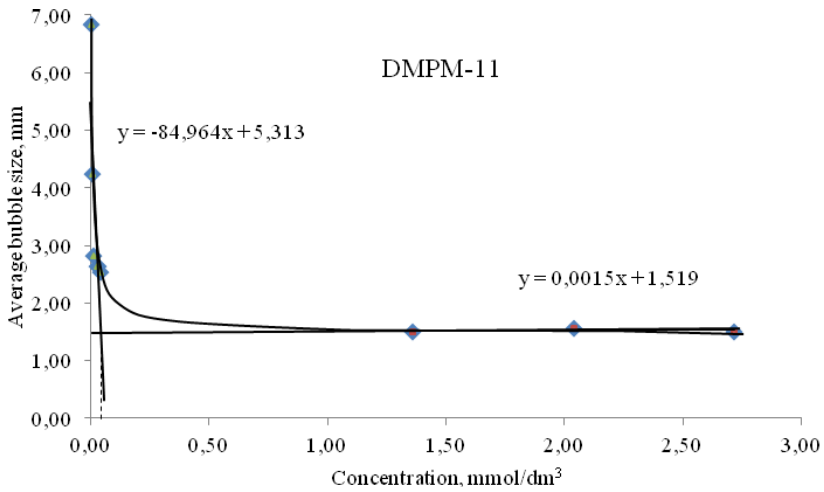
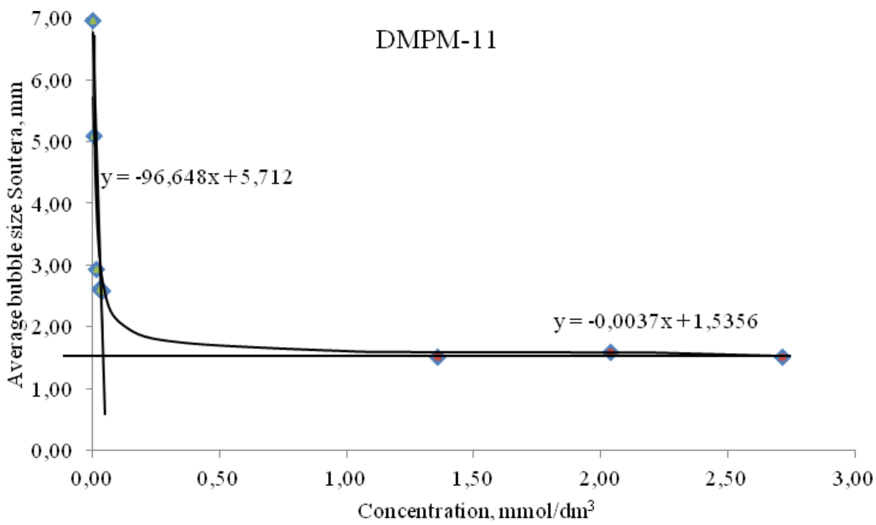


Fig. 9. Critical coalescence concentration (CCC) for DMPM -11



Rys. 10. Critical coalescence concentration (CCC) for DMPM-11

When comparing the CCC values determined for the tested compounds (Tab. 5) it may be noticed that they are similar to 2-dodecanoyloxyethyl) trimethylammonium bromide (DMM-11) (Szyszka, 2006) and for the frothers with long-chain such as polyglicols DF-1012, DF-200 and DF-250, which are used in the industry under the trade name of Dowfroth (Laskowski et al., 2003a,b; Grau et al., 2005; Melo and Laskowski, 2006).

Table 5. Critical coalescence concentration (CCC) values of all tested surfactants

Surfactant	DMGM-12	DMALM-12	DMPM-11
Critical coalescence concentration (CCC), mol/dm^3 (average bubble size)	0.041	0.045	0.048
Critical coalescence concentration (CCC), mol/dm^3 (average bubble size Souter)	0.042	0.043	0.047

3. CONCLUSIONS

In this paper selected cationic surfactants were tested in order to a valuate their possible use as flotation reagents. For this purpose, the critical coalescence concentrations (CCC) of the surfactants were determined. The CCC value represents such a concentration of a reagent at which the air bubbles start to merge, which results in less effective flotation process. Therefore, it is recommended to keep the surfactant concentration in the vicinity of CCC to prevent the occurrence of the coalescence phenomenon.

Basing on the performed research it can be concluded that:

1. plotted graphs show that the coalescence disappears along with the increasing concentrations of the surfactants,
2. for all tested surfactants the values of critical coalescence concentrations (CCC) are similar and are in the range from 0.041 to 0.048 mmol/dm^3,
3. the analysis of both obtained CCC values based on arithmetic and Sauter diameters demonstrates that no considerable variation of the CCC values was observed for the tested surfactants,
4. diameters of air bubbles measured for quaternary ammonium compounds containing a hydrophobic moiety with an ester group and for typical floatation frothers known under the trade name of Dowfroth gave similar CCC values.
5. the CCC values can be an important material constants for foaming agents.

Determination of possibility to use cationic surfactants as flotation frothers and their impact on flotation efficiency should help to select appropriate flotation reagents so that, in addition to typical, already known frothers, other environment-friendly surfactants may be used in mineral processing technology.

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KRYTYCZNE STEŻENIE KOALESCENCJI (CCC) JAKO PARAMETR OCENY CZWARTORZĘDOWYCH ZWIĄZKÓW AMONIOWYCH

Celem pracy było wyznaczenie krytycznego stężenia koalescencji CCC surfaktantów, takich jak: bromek N-(dodecylooksykarboksymetylo)-N,N,N-trimetyloamoniowy (DMGM-12), bromek N-[2-(dodecylooksykarboksy)etylo]-N,N,N-trimetyloamoniowy (DMALM-12) oraz bromek N-[3-(dodekanoylooksy)propylo]-N,N,N-trimetyloamoniowy (DMPM-11). Zastosowane odczynniki to czwartorzędowe związki amoniowe, zawierające hydrofobową grupę zawierającą grupę estrową (powszechnie nazywane, jako „esterquaty"). Określenie wartości krytycznego stężenia polegało na przeanalizowaniu zależności stężenia badanego surfaktantu od średniej średnicy pęcherzyka powietrza. Wartości krytycznego stężenia koalescencji (CCC) określono za pomocą metody graficznej.