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Danuta SZYSZKA[*], Jan DRZYMALA[*], Jacek ŁUCZYŃSKI[**],
Kazimiera A. WILK[**], Jacek PATKOWSKI[***]

CONCENTRATION OF α-TERPINEOL AND (2-DODECANOYLOXYETHYL)TRIMETHYL AMMONIUM BROMIDE REQUIRED FOR PREVENTION OF AIR BUBBLE COALESCENCE IN AQUEOUS SOLUTIONS

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Flotation is a widely used process in mineral processing. It utilizes different reagents including, collectors and frothers. It was proposed by Cho and Laskowski to use the so-called critical coalescence concentration (CCC) for characterization of flotation frothers. In this paper the CCC values were determined for α-terpineol, which is widely used as a frother in laboratory flotation tests, and for (2-dodecanoyloxyethyl)trimethylammonium bromide (DMM-11) which represents a broad family of reagents known as chemodegradable cationic surfactants. The CCC for α-terpineol was found to be 0.16 mmol/dm^3 while for DMM-1, depending of the procedure of approximation, between 0.06 and 0.14 mmol/dm^3.

Key words: critical coalescence concentration, flotation, bubbles, surfactants

INTRODUCTION

In 2002 Cho and Laskowski (2002a,b) introduced a concept of CCC which seems to be an important parameter characterizing surface active reagents. CCC is the concentration of a reagent which prevents bubbles in aqueous solutions from coalescence. The CCC, coupled with the dynamic frothing index (DFI) (Małysa *et al*., 1978, 1982; Czarnecki *et al.*, 1982) is a good base for assessment of surfactants for flotation. According to Laskowski (2004), Grau and Heiskanen (2003) and Grau *et al*.

[*] Wroclaw University of Technology, Department of Geoengineering, Mining and Geology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland.
[**] Wroclaw University of Technology, Department of Chemistry, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland.
[***] UMCS, Department of Radiochemistry and Colloid Chemistry, ul. M.C. Sklodowskiej 3, 20-031 Lublin, Poland.

(2005), selective surfactants are those which have high CCC and low DFI while powerful frothers assume high DFI and low CCC values.

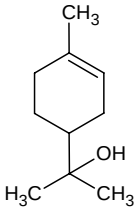
Table 1. CCC for different surfactants (after Laskowski, 2004)

Surfactant	CCC, mmol/dm^3
MIBC (methylisobutylcarbinol)	0.11
(PO)1 (oxypropylene methyl ether)	0.52
(PO)2 (dioxypropylene methyl ether)	0.17
DF-200 (trioxypropylene methyl ether)	0.089
DF-250 (tetraoxypropylene methyl ether)	0.033
DF-1012 (polyoxypropylene methyl ether, n=6.3)	0.015

Thus, the CCC is a useful parameter, but only several surfactants have been investigated so far in order to establish their CCC (Cho *et al*., 2002a,b; Laskowski (2003, 2004). They are presented in Table 1. The goal of this research is to determine the CCC for two reagents, which represent two different families of surfactants. The first one is α-terpineol which is widely used as frother in laboratory flotation tests for ores and raw materials. The other surfactant is (2-dodecanoyloxyethyl) trimethylammonium bromide (denoted as DMM-11) and it represents a broad family of reagents known as chemodegradable cationic surfactants (Wilk *et al.,* 1994). The structures of the investigated surfactants are given in Table 2.

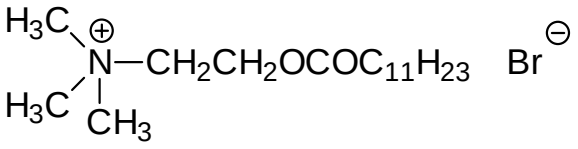
Table 2. Structures of the investigated surfactants

α-terpineol



(CAS 98-55-5)

DMM-11



(CAS 25234-60-0)

EXPERIMENTAL

MATERIALS

α-terpineol ($C_{10}H_{18}O$ or dl-p-menth-1-en-8-ol) and DMM-11 ($C_{17}H_{36}BrNO_2$ or (2-dodecanoyloxyethyl)trimethylammonium bromide were tested. α-terpineol was purchased from Fluka while the DMM-11 surfactant was synthesized in the Department of Chemistry of Wroclaw University of Technology starting from N,N-dimethylaminoethyl ester of dodecanoic acid (Łuczyński, 2000) and then by quaternization in an ethereal solution using methyl bromide (Obłąk *et al*, 2001). The t_m of DMM-11 is 135 – 140 ^oC while the CMC is $5.9 \cdot 10^{-3}$M. Then, the obtained salt was purified by a repeated crystallization, first from the $CHCl_3$ – n-hexane mixtures,

and next from the methanol–diethyl ether mixtures. A high purity of DMM-11 was proved by elementary analysis, surface tension measurements, and NMR data.

The stock solution of α-terpineol contained 0.05 wt.% of the frother while DMM-11 was used from daily prepared aqueous solutions.

α-terpineol was dissolved in distilled water by applying vigorous stirring for 16 h at 40°C while no special procedure of dissolution was applied for DMM-11 which easily dissolves in water. Some additional properties of the surfactants used in the experiments are given in Table 3. Double distilled water was used in all experiments.

Table 3. Selected properties of surfactants used in this study (at 25°C)

Property	α-terpineol	DMM-11
Chemical formula	$C_{10}H_{18}O$	$C_{17}H_{36}BrNO_2$
Supplier	Fluka	Chemistry Department of The Wroclaw University of Technology
Molecular weight (g/M)	154.25	326.00
Physical state	solid	solid
Solubility, g/dm^3	1.987	no limit
Density, g/cm^3	0.948	not determined

Methods

Bubbles have been generated in an open rectangular cell of 89 cm^3 in volume (Fig. 1). They have been generated with a small plastic tube at an airflow rate of about 5 dm^3/min. This procedure was applied for different concentrations of the surfactants. The process of bubble formation along with the bubbles approaching the water-air interface was photographed and recorded with a digital camera. Six frames containing at least 50% of well shaped and visible bubbles were chosen from each recorded experiment. The photographs were later used for bubble diameter measurements. The average size of the bubbles was calculated as an arithmetical mean for all (usually ~200) bubbles seen in the photograph.

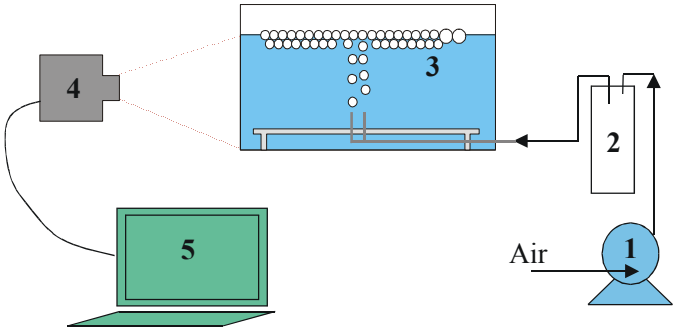


Fig. 1. Experimental set-up for CCC measurements:
1) peristaltic pomp, 2) equalizing tank, 3) cell, 4) digital camera, 5) computer

RESULTS AND DISCUSSION

Figures 2 and 3 show the size of bubbles as a function of surfactant concentration for α-terpineol and DMM-11, respectively. Figures 2a and 3a present the bubble in distilled water. At higher frother concentrations (c >> CCC) the size of bubbles becomes constant and equal to the size of the original, newly formed, bubbles. Near and below the CCC, the bubbles undergo coalescence, their size increases and the foam formed by the surfactants is very unstable. The foam exists only during the bubbling the gas through the solution and collapses when the percolation is stopped. Figures 4 and 5 provide the critical coalescence concentration (CCC) determined by a graphical method similar to that used for the CMC determination.

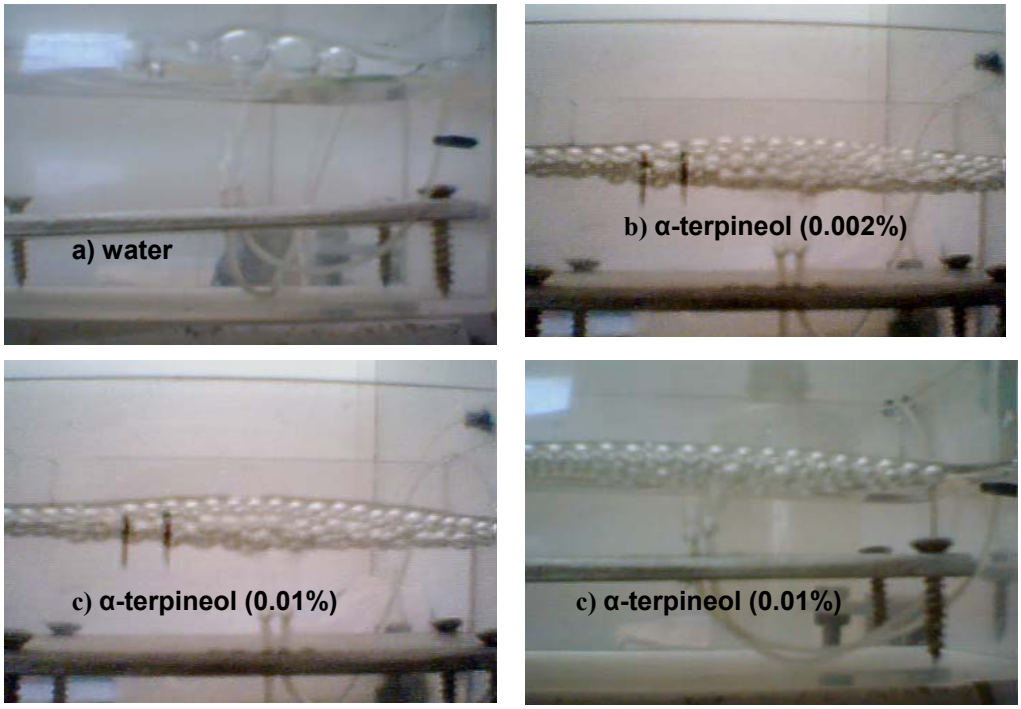


Fig. 2. Bubbles formed in aqueous solutions containing α-terpineol: a) 0%, b) 0.002%, c) 0.01%, and d) 0.05% (wt %)

According to Figs 4 and 5, the CCC value for α-terpineol is about 0.16 mmol/dm^3 while for DMM-11 is above 0.05 mmol/dm^3, that is, depending on the procedure of approximation, somewhere between 0.06 and 0.14 mM. A comparison of the CCC values of the investigated here surfactants with those characterized by Laskowski *et al.* (2004) shows, that the CCC for α-terpineol is closed to that of MIBC, while for DMM-11 is similar to that of polyoxypropylene methyl ether frothers with n between two ((PO)2) and three (DF-200).

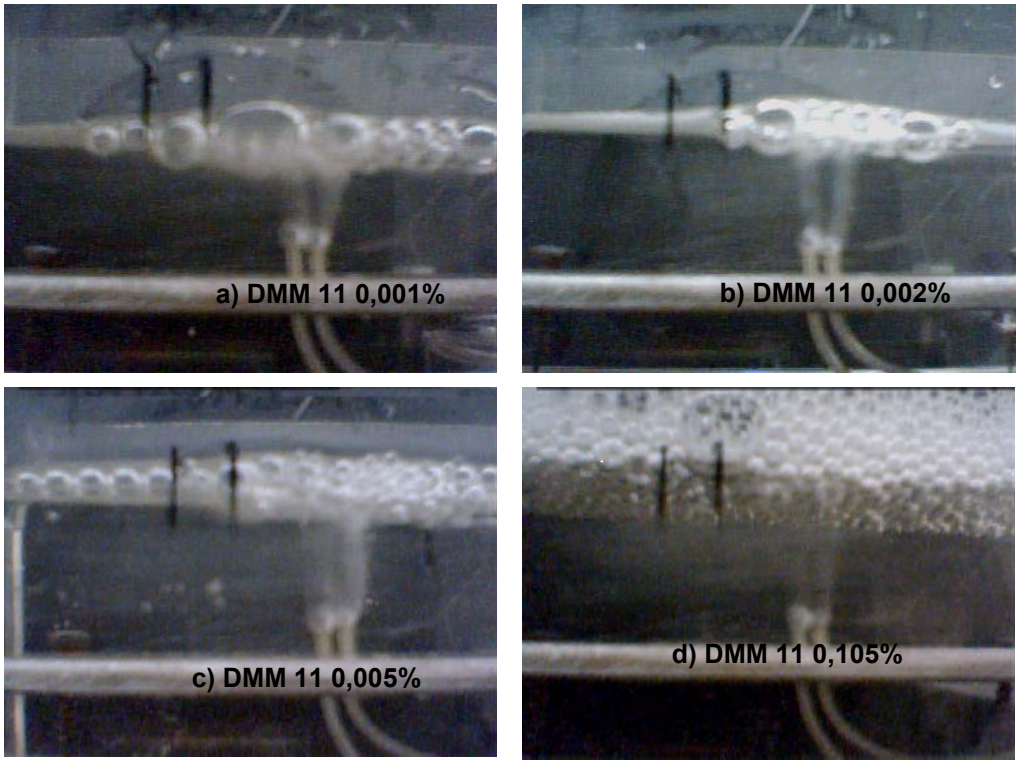


Fig. 3. Bubbles formed in aqueous solutions containing DMM-11: a) 0%, b) 0.002%, c) 0.005%, and d) 0.105%

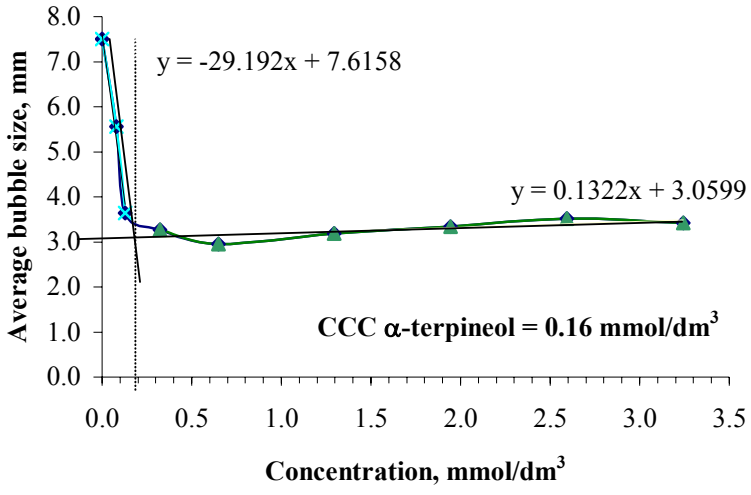


Fig. 4. Critical coalescence concentration (CCC) for α-terpineol

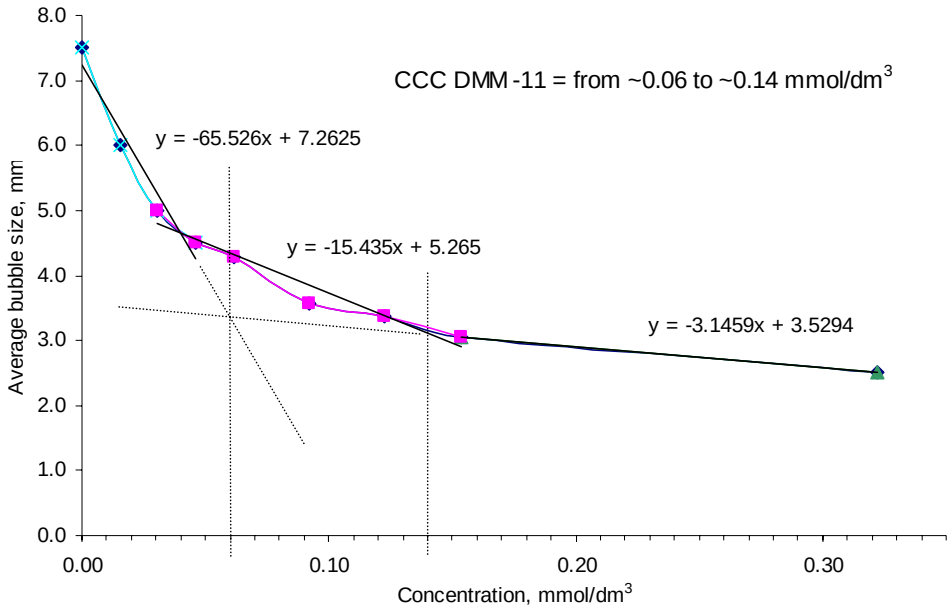


Fig. 5. Critical coalescence concentration (CCC) for DMM-11

CONCLUSION

The CCC of α-terpineol is about 0.16 mmol/dm^3 and the CCC of DMM-11 is somewhere between 0.06 and 0.14 mmol/dm^3.

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Flotacja jest jednym z najczęściej stosowanych procesów w mineralurgii. Wśród najważniejszych czynników flotacji są reagenty, a w szczególności stosowane odczynniki pianotwórcze (spieniacze). W celu charakteryzowania spieniaczy flotacyjnych Cho i Laskowski wprowadzili pojęcie krytycznego stężenia koalescencji (CCC). W pracy wyznaczano CCC dla typowego spieniacza stosowanego w procesie flotacji, jakim jest α-terpineol oraz dla DMM-11 reprezentującego surfaktanty z grupy chemodegradowalnych estrów kationowych. Stwierdzono, że CCC dla α-terpineolu wynosi 0.16 mmol/dm^3, podczas gdy dla DMM-11, w zależności od sposobu aproksymacji, wynosi ono od 0.05 do 0.15 mmol/dm^3.