Development of a UV-spectrophotometric method for analysis of esterquats-containing flotation collectors in aqueous solutions

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Abstract In this study a rapid and simple UV spectrophotometric method was developed and validated for the quantitative determination of the esterquats-containing flotation collector FLOT 2015 in aqueous solutions. The method is based on the formation of an ion pair by FLOT 2015 and Bromocresol purple (BCP), an anionic dye, and the subsequent measurement of the reduction in absorbance without extraction by organic solvents. The optimum conditions for FLOT 2015 detection and analysis were established. Sample solutions were stable up to three hours. The absorbance maximum was obtained at 574 nm. The proposed method showed the linearity in the range of 5-45 μg/mL with the correlation coefficient of 0.9917. Standard and relative standard deviation obtained by intra- and inter-day precision tests of the proposed method were within the permissible bias range and considered satisfactory. The method was found to be selective and specific for successful determination of FLOT 2015 in aqueous flotation systems.

Keywords Esterquats, UV Spectrophotometry, Quantitative determination, Liquid flotation dosage form

Introduction

Esterquats are cationic surfactants with the general formula $R_4N^+X^-$. Due to their unique structure with the ester bond located between the quaternary ammonium group and the hydrocarbon chain esterquats can be decomposed into non-surface-active fragments through a hydrolysis process (Hellberga et al., 2000; Overkempe et al., 2005). The initial protonation of the ester carbonyl group hindered by the positively charged nitrogen causes slow acid-catalysed hydrolysis while base-catalysed hydrolysis is faster than with normal esters (Federle et al., 1997; HERA, 2008; Para et al., 2015; Kronberg et al., 2017). Esterquats usually biodegrade more rapidly compared to the related alkylquats, show low toxicity and can be considered as cleavable and more environmentally friendly reagents. Current legislation obligates industry to replace harmful reagents with more environmentally friendly alternatives when possible. This acts as a driving force in the development of green flotation chemicals. Omya Hustadmarmor AS, Elnesvågen, Norway, initiated the process of introduction of esterquats-containing reagent FLOT 2015 as a cationic collector with improved environmental characteristics in reverse flotation to remove silicates from calcite in the production of high purity calcite filler. FLOT 2015 comprises a mixture of reaction products of fatty acids, C16-18 and C18-unsaturated, with triethanolamine, di-methyl sulfate-quaternized (TEA-esterquat) dissolved in 20-30% isopropanol (Hylland et al., 2014). Table 1 shows the structures, molecular formulas and molecular weights of three main components of FLOT 2015.

However, due to the complexity of the reagent, its very pH dependent and time limited stability, FLOT 2015 does not appear to have been extensively tested with regard to physiochemical properties and quantification of the main components in aqueous medium. Recently published studies indicate that analytical methods have not been completely successful to determine esterquats in complex mixtures and in very low concentrations (Mishra et al., 2007; Weng et al., 2014). Nevertheless, there are methods to quantify the substances such as Time-of-Flight Mass Spectrometry with quadrupole filter technology (Wulf et al., 2010), High Performance Liquid Chromatography with spectrophotometric detection (Chung et al.,1998; Bahmaei et al., 2011) or Mass Spectrometry (Levsen et al., 1993). In addition, UV-spectrophotometry is a suitable analytical technique of choice in research and industrial laboratories due to its inherent simplicity, portability and low cost (Wigman et al., 1989). The direct measurement of the UV absorbance of amine based flotation reagents is only feasible when the reagents contain aryl groups giving them strong UV absorptivity.

Almost all of the colorimetric methods are based on the formation of an ion pair between the cationic surfactant and an anion, in this case a dye. The ion pair is extractible into an organic solvent, while the dye alone is not, so the colour of the organic phase is directly proportional to the surfactant concentration (Water et al., 1976; Wyrwas et al., 2017). This approach is suitable for determination of low concentrations and has been used frequently for environmental studies. However, these methods are often suffering due to formation of emulsion in the solvent or incomplete extraction which diminishes precision and accuracy. Addition of a cationic surfactant to an aqueous solution of an anionic dye results in a change of maximum light absorbance, observed as a decrease in intensity of the dye colour. It can be used as a means of determining low levels of cationic surfactants which does not require extraction of ion pairs into an organic solvent. While most of the anionic dyes can give adequate results with cationic surfactants over a wide range of pH, some of them show better sensitivity than others for determination of individual surfactants (Chatten et al., 1973; Bonilla Simon et al., 1990). The principles of UV-spectrophotometry were applied for the determination of cationic surfactants without extraction using azo dyes of the methyl orange series in acidic medium (Motomizu et al., 1992; Akbas et al, 2005), Bromothymol blue, Bromocresol purple and Bromocresol green buffered at pH 8 (Yamamoto et al., 1991; El-Khateeb et al, 1998; Didamony et al., 2010). In the case of esterquats, the development of a sensitive and simple method for the quantification of the complex systems with several active ingredients still constitutes a major challenge.

The aim of the study is to develop and evaluate a simple and adequate UV-spectrophotometric method for the determination of esterquats-containing reagent FLOT 2015 and build successful testing schemes for its quantitative analysis in aqueous systems.

Experimental

Instruments and Apparatus

UV-vis spectra were recorded on a DR3900 Laboratory VIS Spectrophotometer (HACH – Lange GmbH, USA), with wavelength range 320–1100 nm, spectral bandwidth 5.0 nm, wavelength resolution 1 nm, with 10 mm matched quartz cells.

Reagents and Chemicals

The industrial reagent FLOT 2015 and polymer-based flocculant FLOC 2014 were obtained from Omya Hustadmarmor AS, Elnesvågen, Norway. Bromocresol Purple (BCP) was purchased from Sigma Aldrich Co., Schnelldorf, Germany. Methyl isobutyl carbinol (MIBC) was obtained from BASF Co., Norway. Phosphate buffer solution (0.1 M) was used to adjust the pH of reaction solutions to 7. All single chemicals were of analytical-reagent grade and used without further purification.

Sample preparation and analysis

A stock solution of FLOT 2015 was prepared by dissolving 1 g of the reagent in 20 mL of ethanol and then made up 1000 mL with distilled water. BCP stock standard solution ($1.25 \cdot 10^{-4}$ M) was prepared by dissolving accurately weighed amounts of the dye in 10 mL of 0.01 M sodium hydroxide solution and diluting to 100 mL with distilled water.

Aliquots of stock solution (1g/L) were transferred into a set of 100 mL volumetric flasks and volumes made up to the mark with distilled water to produce solutions in the concentration range 1-120 μg/mL.

1 mL of $1.25 \cdot 10^{-4}$ M dye solution, 1 mL of 0.1 M buffer solution and 2 mL of FLOT 2015 solution were pipetted into a 10 mL volumetric flask, diluted to the mark with distilled water and mixed thoroughly. The adsorption spectra of the sample solution and the reagent blank solution without FLOT 2015 were measured against distilled water. Absorbance was measured at 574 nm against the reagent blank.

Analytical method validation

Validation is a process to establish the documentary evidence, which provides a high degree of assurance that the method is performing consistently to produce a desired result, or a product meeting its predetermined specifications and quality characteristics. The method was validated for Linearity, Accuracy, Precision, Specificity, Sensitivity, Limit of Detection (LOD), and Limit of Quantification (LOQ) (Miller, 1995; Patel et al., 2011).

Results and Discussion

Linearity and range

Aqueous solutions of the system BCP-FLOT 2015 were measured at 574 nm against the BCP reagent with distilled water as a blank and corresponding UV spectrum of BCP is shown in Figure 1. A calibration curve, which showed a linear response, was constructed by plotting the change in absorbance of BCP versus the concentration of FLOT 2015 (Figure 2). The linear regression analysis of calibration data gave the regression results shown in Table 2 with correlation coefficients close to unity. The linearity of samples can be observed in Table 3. The linear dynamic range of FLOT 2015 was found to be 5-45 μg/mL (mg/L).

Accuracy and Precision

The accuracy of the proposed method was determined by preparing samples of different concentrations with the different levels of addition such as 50, 80, 100, 120%. The amount of FLOT 2015 was kept constant 20 μg/mL and the amount of the new solutions were varied, that is, 10, 16, 20 and 24 μg/mL for 50, 80, 100 and 120 %, respectively. Table 4 shows the accuracy of the proposed method by recovery. The recovery values were calculated by dividing the measured concentration by the known total concentration.

Precision was estimated through intraday and interday tests by determining the content of FLOT 2015 in bulk samples at different concentration levels. In the intraday experiments different samples of the same concentration (25 μg/mL) were prepared and analyzed three times a day. The results are expressed indicated by SD and RSD in Table 5. Interday tests were conducted measuring the absorbance of the fresh solutions of the same concentration for three consecutive days and then the change in absorbance was calculated (Table 6).

The standard deviation, relative standard deviation obtained by proposed method are within the permissible bias range and can be considered satisfactory.

Sensitivity and Specificity

The sensitivity of the method was evaluated by estimating the limit of detection (LOD) and limit of quantification (LOQ) for the BCP-FLOT 2015 system. LOD and LOQ were determined by injection of a series of diluted solutions with known concentration of FLOT 2015. LOD is defined as the lowest concentration that can be detected. LOD for FLOT 2015 was found to be 1 μg/mL. LOQ is the lowest concentration of the addition that can be measured with acceptable precision and accuracy. LOQ for FLOT 2015 was found to be 2 μg/mL. Results are shown in Table 7.

Mineral processing systems are complex and can include the use of collectors, activators, depressors, frothers, flocculants, etc. Hence, a variety of chemical components can be found in the aqueous solution. Omya Hustadmarmor AS uses organic polymeric flocculant FLOC 2014 which comprises the mixture of hydrogenated light petroleum distillate and fatty alcohol ethoxylate and shows a remarkable ability to flocculate particles efficiently at a low dosage. Therefore, the specificity of the proposed method was proven by injecting solutions of FLOC 2014 that was expected to be present in the system prior to submarine tailings deposition. The influence of FLOC 2014 was studied by mixing the FLOT 2015 solution (25 μg/mL) with FLOC 2014 of different concentrations such as 1, 2, 5 and 10 μg/mL, then the resulting solutions were mixed with BCP and the samples were analysed (Table 8). As seen from Table 8, the addition of FLOC 2014 did not cause significant interference on BCP-FLOT 2015 complex formation and change in absorbance of BCP.

And it is also, although esterquats-containing reagents have foaming properties, the frothers are using to improve the performance. MIBC is 4-methyl-2-pentanol and stabilizes the froth in reverse flotation of silicates. Thus, in order to demonstrate the broader set of reagents, which can be co-used with FLOT 2015, the selectivity of the method was proven by injecting solutions of MIBC. The interference of MIBC on FLOT 2015 determination was studied by mixing the FLOT 2015 solution (25 μg/mL) with MIBC of different concentrations such as 1, 2, 5, 7, 10 and 20 μg/mL, then the resulting solutions were mixed with BCP and the samples were analysed (Table 9). Table 9 shows no significant change in BCP absorbance and indicates the reliable selectivity of the proposed method.

Solution stability

Solution stability tests were carried out by keeping the standard solutions of different concentration of FLOT 2015 in standard flasks at room temperature for 6 hours. The samples were analysed at 1 hour interval up to 6 hours. No significant change was observed within the first 3 hour period. Then the stability of the FLOT 2015 solutions decreased rapidly due to extensive hydrolysis.

Conclusion

The UV-spectrophotometric methods are of beneficial interest in flotation reagents quantification since they offer the possibility in rapid assessment of the concentration of components in aqueous systems prior to tailings deposition. This is crucial for environmental impact analysis. In the present study a simple, rapid, low cost and reliable UV-spectrophotometric method for quantitative analysis of esterquats-containing reagent FLOT 2015 was developed and validated. The optimum conditions for FLOT 2015 detection were established. The proposed method showed the linearity in the range of 5-45 μg/mL with the correlation coefficient of 0.9917. Standard and relative standard deviation obtained by intra- and inter-day precision tests of the proposed method were within the permissible bias range and considered satisfactory. The method was found to be selective and specific for successful determination of esterquats-containing flotation reagents and can be applied efficiently in aqueous mineral processing systems when time and economy are essential.

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Table 1 Structures, molecular formulas and molecular weight of the main components of FLOT 2015

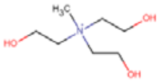
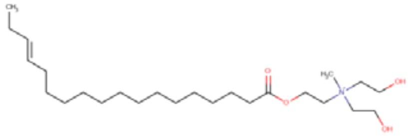
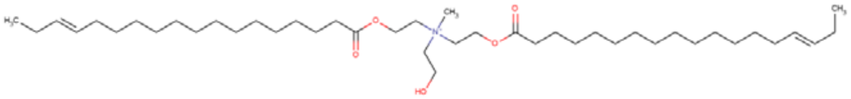
Name and structure	Molecular formula	Molecular weight, g/mol
tris (2-hydroxyethyl) (methyl) azanium (QAC) 	$C_7H_{18}NO_3$	164.128
bis(2-hydroxyethyl) (methyl){2-[(15E)-octadec-15-enoyloxy] ethyl}azanium (monoester) 	$C_{25}H_{50}NO_4$	428.373
(2-hydroxyethyl) (methyl)bis {2-[(15E)-octadec-15-enoyloxy]ethyl}azanium (diester) 	$C_{43}H_{82}NO_5$	692.618

Table 2 Validation parameters

N	Parameter	Result
1	Absorption maximum	574 nm
2	Linearity range	5-45 µg/mL (mg/L)
3	Standard regression equation	y=0.0035x
4	Correlation coefficient R^2	0.9917
5	Standard deviation (SD)	0.003229
6	Relative standard deviation (RSD)	0.644752

Table 3 Linearity of the working solutions

Concentration of FLOT 2015, µg/mL	Change in absorbance	Standard deviation
0	0	0
10	0.03125	0.002986
20	0.06625	0.001893
25	0.088	0.003697
30	0.1065	0.003916
35	0.1195	0.002944
40	0.1285	0.007118
42	0.1365	0.000816
44	0.16025	0.003055
45	0.16725	0.006397
50	0.407	0.004203
55	0.5335	0.003162
60	0.60075	0.0005

Table 4 Determination of accuracy of the proposed method

Initial concentration of FLOT 2015, µg/mL	Level of addition, %	Amount of FLOT 2015 added, µg/mL	Total concentration of FLOT 2015, µg/mL	Concentration of FLOT 2015 found, µg/mL	Recovery, %	Mean recovery+SD, %
20	50	10	30	29.43	98.1	98.59+1.6
20	80	16	36	35.57	98.81	
20	100	20	40	38.71	96.78	
20	120	24	44	44.28	100.65	

Table 5 Intraday precision results for FLOT 2015

Concentration of FLOT 2015, µg/mL	Change in absorbance	Mean +SD	RSD,%
25	0.088	0.089583+ 0.00196	2.19
25	0.0915		
25	0.087		
25	0.092		

25	0.090		
25	0.089		

Table 6 Interday precision results for FLOT 2015

Concentration of FLOT 2015, 25 µg/mL	Change in absorbance	Mean +SD	RSD,%
Day 1	0.089	0.089333+ 0.002517	2.82
Day 2	0.092		
Day 3	0.087		

Table 7 Summary of sensitivity tests of the proposed method

Initial concentration of FLOT 2015, µg/mL	Amount of FLOT 2015 added, µg/mL	Total concentration of FLOT 2015, µg/mL	Concentration of FLOT 2015 found, µg/mL	Recovery,%
25	2.5	27.5	28.86	104.95
25	5	30.0	30.02	100.00
25	10	35.0	35.43	101.23
25	15	40.0	41.14	102.85

Table 8 Test 1 for specificity

Concentration of FLOT 2015, µg/mL	Concentration of FLOC 2014 added, µg/mL	Change in absorbance	Concentration of FLOT 2015 found after addition, µg/mL	Total FLOT 2015 recovered, %	Mean recovery,%
25	0	0.0875	25.00	100.00	98.31
25	1	0.088	25.12	100.48	
25	2	0.086	24.86	99.44	
25	5	0.085	24.35	97.40	
25	10	0.084	23.98	95.92	

Table 9 Test 2 for specificity

Concentration of FLOT 2015, µg/mL	Concentration of MIBC added, µg/mL	Change in absorbance	Concentration of FLOT 2015 found after addition, µg/mL	Total FLOT 2015 recovered, %	Mean recovery,%
25	0	0.087	25.00	100.00	99.2
25	1	0.0885	25.43	101.72	
25	2	0.0873	25.08	100.32	
25	5	0.0869	24.97	99.88	
25	7	0.085	24.42	97.68	
25	10	0.0865	24.85	99.4	
25	20	0.0835	23.99	95.96	

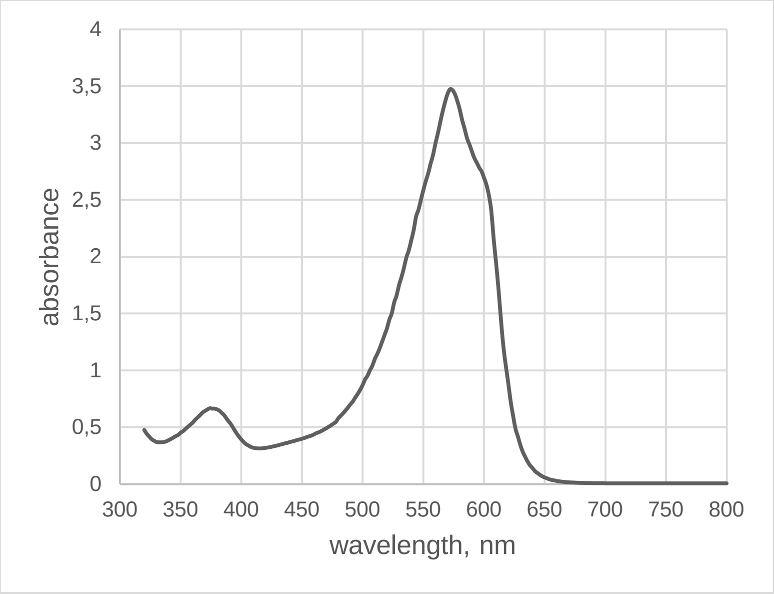


Fig. 1 UV spectrum of BCP in distilled water (1.25x10^{-4} M)

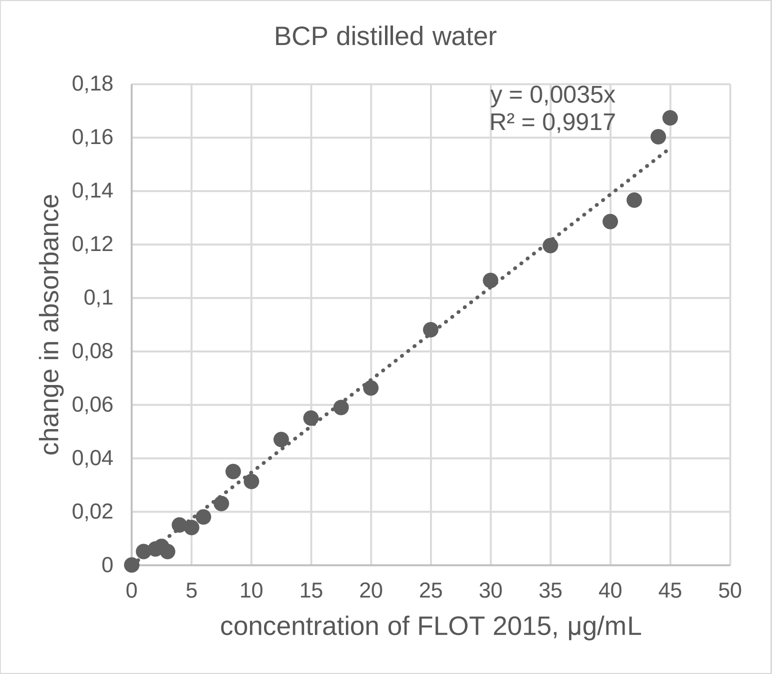


Fig. 2 Linearity of change in absorbance corresponding the concentration of FLOT 2015