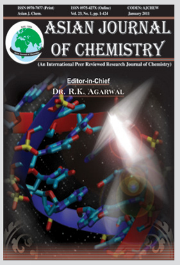
Asian Journal of Chemistry; Vol. 23, No. 10 (2011), 4464-4466

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Determination of Trace Amounts of Benzalkonium Chloride by Liquid-Liquid Extraction-Spectrophotometry Method

Z. GH. AFSHAR* and H. PARHAM

Department of Chemistry, Omidieh Branch, Islamic Azad University, Omidieh, Iran

*Corresponding author: Fax: +98 652 3222533; Tel: +98 652 3223434; E-mail: afshar_ghz@yahoo.com

(*Received*: 22 November 2010; *Accepted*: 24 June 2011) AJC-10074

This study describes a simple, sensitive and selective extraction-spectrophotometric method for the determination of trace amounts of cationic surfactant of benzalkonium chloride. The benzalkonium-orange II ion-pair in bufferic media is quantitatively extracted into chloroform and its absorbance is measured at 487 nm at room temperature. The effect of different variables such as solvent, volume of extracting solvent, volume of anionic reagent, pH, ionic strength (0.4 M NaCl) and shaking time is investigated and optimum conditions for quantitative extraction of benzalkonium is obtained. Linear calibration graph over the benzalkonium chloride concentration rang 0.25-9.0 µg mL^{-1} and regression coefficient of 0.9999 is obtained. The relative standard deviation of ten replicate determinations of 5 µg mL^{-1} of benzalkonium chloride is 0.959 %. Limit of detection of the method is 0.054 µg mL^{-1}. The interfering effect of 20 a large number of diverse ions on the determination benzalkonium chloride was studied. The method is used for determination of benzalkonium chloride in the washing solution vegetable and good results are obtained.

Key Words: Benzalkonium chloride, Liquid-Liquid extraction, Spectrophotometry, Quaternary ammonium.

INTRODUCTION

Benzalkonium chloride (BZC) consists of a mixture of [N-benzyl-N, N-dimethylalkan-1-chloride][1] is a quaternary ammonium compound and is a part of cationic surfactants[2] (Fig. 1), alkyl benzyl dimethyl ammonium chlorides are with the general formula $[C_6H_5CH_2N(CH_3)_2R]Cl$ where $R = n\text{-}C_8H_{17}$ to $n\text{-}C_{19}H_{39}$[3], which differ in the length of the *n*-alkyl chain (C_{12}, C_{14}, C_{16} *etc.*)[4]. The microbiological activity differs in the length of the *n*-alkyl chain. The C_{12}, C_{14} and C_{16} chains comprise the major portion of the alkyl mixture[3]. It is well known that the C_{12}-homolog is most effective against, the C_{14} homolog against gram-positive bacteria and the C_{16} homolog against gram- negative bacteria[3-5]. Benzalkonium salts are an important class of cationic surfactants with both industrial and commercial uses. These environmentally friendly antibacterial agents degrade relatively rapidly into non-toxic and inactive products after they have had their desired effect[1]. It is used to preserve otic, nasel and parenteral formulations as well[6]. Because of their strong cationic surface activity, quaternary compounds are used primarily as disinfectants, biocides and detergents[7]. Very important features of benzalkonium salts are their bactericidal and antimicrobial properties. The antimicrobial activity depends on a changing length of the side *n*-alkyl chain[3]. Several works have been reported for the quantitative determination of cationic surfactants in water sample[8-18]. Among them, solvent extraction[8,9], HPLC[10] and capillary electrophoresis[11] methods are not applicable for the analysis of cationic surfactants in environmental samples due to the interference from anionic surfactants. Flow injection analysis[12] is simple and rapid, but the sensitivity is still very poor[19]. GC/MS and LC/MS are used for determination of cationic surfactants in river water and sewage effluent, respectively[14,15]. These two methods were highly sensitive, but tedious and time-consuming and only applicable to alkyl dimethyl benzyl ammonium ion[19]. Analytical methods using ion-pair as the liquid-liquid extraction media have been developed in recent years[9]. Amoung them extraction of cationic surfactant CTAB in antidandruff samples with chloroform as the solvent was reported in previous work[9] and recent study showed that one of the cationic surfactants benzalkonium chloride determined by spectrophotometry

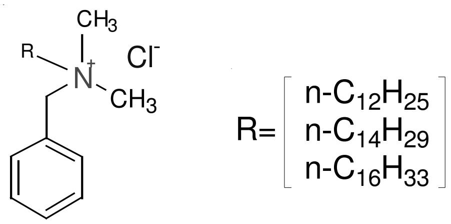


Fig. 1. Structure of benzalkonium chloride

method. Now the goal of this work is to describe a simple, sensitive, easily repeatable and low cost method for the determination of benzalkonium chloride (BZC). In this study the extraction process is based on formation of ion-pair between BZC and a suitable indicator dye RSO_3Na for the quantitative extraction of BZC ion-pair from a buffer solution into organic solvent followed by UV-VIS spectrophotometric measurements. The mechanism of the formation ion-pair is shown by:

$$BZC \rightarrow BZ^+ + Cl^-$$
$$RSO_3Na \rightarrow RSO_3^- + Na^+$$
$$BZ^+ + RSO_3^- \rightarrow BZ^+RSO_3^-$$

When hydrophobic ions are dissolved in water, they are weakly hydrated. These ions are easy to form ion associated with hydrophobic counter ions through hydrophobic interaction. When the water solution add to a little amounts of organic solvent, the ion associates $BZ^+RSO_3^-$ are transfered easily to the organic phase by shaking.

EXPERIMENTAL

All chemicals used in this study were obtained from Merck. Purity of all products was tested by determination of their melting points. Double distilled deionized water was used throughout. 50 µg mL^{-1} stock solution of benzalkonium chloride was prepared by dissolving 0.05 g of BZC (Merck) powder in water and diluting to the mark in a 1000 mL volumetric flask. Working solutions were prepared by appropriate dilution of the stock solution with water. Orange(II), methyl orange and methyl red stock solution (5.0×10^{-4} M) were prepared by dissolving 0.0175, 0.0164 and 0.0135 g of dyestuff (Merck) in water and diluting to the mark in three 100 mL volumetric flasks respectively. Sodium chloride stock solution (0.4 M) was prepared by dissolving 11.7 g of the NaCl (Merck) in water and diluting to the mark in a 500 mL volumetric flask.

The absorption spectrum was recorded on a JENWAY model 6505 recording spectrophotometer and was used for absorbance measurements. All pH measurements were made by a metrohm digital pH meter equipped with a combined glass electrode.

Recommended procedure: An aliquot of sample solution containing 0.25-9.0 µg of BZC (50 µg mL^{-1}) was placed in a 10 mL of volumetric flask. 1 mL of orange II solution (5×10^{-4} M), 1 mL of 0.4 M of NaCl solution and 2 mL of buffer solution (pH = 9) were added and the solution was diluted to the mark with distilled water. The solution was transferred into a 50 mL separating funnel and 3 mL of chloroform solvent was added. The solution was shaken vigorously for 1 min. The phases were allowed to separate and the organic phase absorbance was measured at 487 nm against a reagent blank. In order to determine the quantity of quaternary ammonium surfactant BZC in a solution was prepared and tested according to the recommended procedure. The test was carried out covering concentrations with in the linear dynamic ranges of the species.

RESULTS AND DISCUSSION

In order to obtain best results and more sensitive method different factors were optimized.

Choice of anionic colour: Selection of the anionic dye is very important in this study. The dye should give lower reagent blank, higher sensitivity and better extraction of ion-pair on the organic phase. In preliminary experiments it was found that the counter anion plays an important role in the formation of a stable ion-pair and among dyestuffs examined such as methyl red, methyl orange and orange II and best results were obtained with orange II dyestuff. Since BZ^+ cation forms a fairly stable 1:1 ion-pair with orange II in organic solvents, application of an anionic dyestuff as counter ion was expected to result in a sensitive and useful spectrophotometric method for trace BZ^+ cation determinations. The effect of orange II concentration on the extraction of ($BZ^+RSO_3^-$) ion-pair was examined and the results showed that optimum concentration of orange II is (1 mL, 5×10^{-4} M) in the final solution (Fig. 2). A further excess of both reagents has no considerable effect on the measured absorption, except that in the case of orange II the absorbance of the blank solution tends to increase gradually.

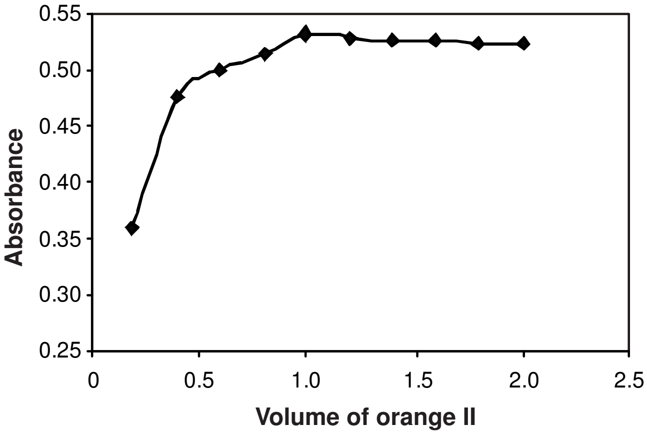


Fig. 2. Effect of volume of orange II on the extraction of ($BZ^+RSO_3^-$) ion pair

Choice of organic solvent: The extraction process was performed under optimal conditions with some common organic solvents such as dichloromethane, chloroform and carbon tetrachloride. It was found that the ion-pair is readily extractable in chloroform, while in other solvents used, the coloured complex could not be extracted into the organic phase as completely as chloroform.

Effect of organic solvent volume: It must be mentioned that quantitative extraction of ($BZ^+RSO_3^-$) ion-pair is complete by 3 mL of chloroform in a single stage extraction process. This was confirmed by observing further enhancement in the absorption of ion pair in the mixture of two 3 mL portions of the organic phase obtained from two successive extractions of an aqueous ($BZ^+RSO_3^-$) ion-pair solution, compared with that of an only 3 mL organic phase obtained from a single stage extraction of the same solution under optimal experimental conditions.

Effect of buffer solution: We added buffer solution to the sample and blank after the addition of orange II solution to form state ($BZ^+RSO_3^-$) ion-pair that could be easily extracted on the organic phase solution. The effect of pH on the extraction was studied in the pH range of 3-11 and best results were obtained at pH = 9 with 2 mL buffer NH_3/HCl 0.1 M.

Effect of ionic solution: In order to best and rapid separation of two aqueous and organic phases, from other, we used 1 mL of NaCl (0.4 M).

Effect of shaking time: The effect of shaking time on the extraction of ($BZ^+RSO_3^-$) ion-pair was studied. A shaking time of 60 s was found to be sufficient for the extraction of ion-pair (Fig. 3).

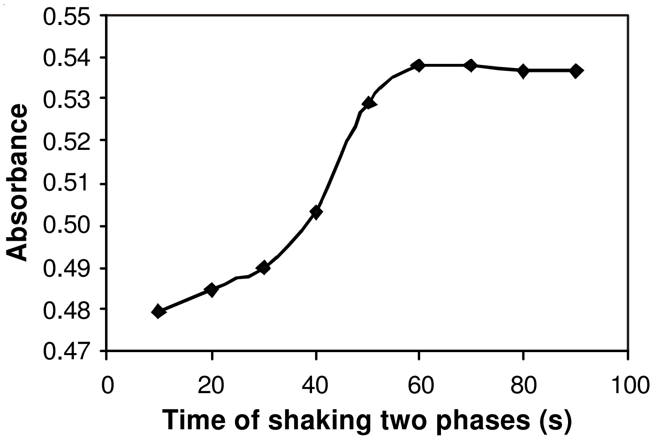


Fig. 3. Effect of shaking time on the extraction of ($BZ^+RSO_3^-$) ion pair

Analytical performance: Under the optimum condition described above, linear calibration graph for BZC was obtained in the concentration range of 0.25-9.0 μg mL^{-1}, the regression equation for BZC is $A_{BZC} = (0.1504\ C_{BZC} - 0.0048)$ with correlation coefficient of 0.9999 (where A_{BZC} is the absorbance of the sample against a blank solutions and C_{BZC} is the concentration of BZC in μg mL^{-1}). RSD of ten replicate measurements is 0.959 % for 5 μg mL^{-1} of BZC ion solution. The limit of detection (LOD), of the method is estimated to be 0.054 μg mL^{-1}.

Effect of diverse ions: In order to study the influence of various cations and anions on the determination of BZC, a fixed concentration of BZC, 5 μg mL^{-1}, was taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of ± 3 % with respect to the absorbance of primary ion solution was considered tolerable. The results are summarized in Table-1, with maximum tolerance limit for each ion.

TABLE-1
EFFECT OF FOREIGN IONS ON
DETERMINATION OF BZC (5 μg mL^{-1})

Species	Tolerance limit of ion to BZC
Cu^{2+}, Ni^{2+}	1000
SCN^-	900
Zn^{2+}, Ca^{2+}, SO_3^{2-}, CO_3^{2-}, CrO_4^{2-}, F^-	800
Ba^{2+}, Pb^{2+}, Li^+, Cl^-, NO_2^-	700
Fe^{2+}, Na^+, $S_2O_3^{2-}$, IO_3^-, I^-	600
Mg^{2+}	500

Application: The proposed method was applied to the determination of BZC in a sample of washing solution of vegetable. As it is seen, there is a satisfactory agreement between the results of the proposed method and BZC standard solution determination.

Conclusion

The method described, provides a simple and reliable means of determination of trace amount of BZC in real samples. The limit of detection of the proposed method is much better compared with some previously reported methods. The method compares favourably in sensitivity and selectivity with most of the published methods for determination of BZC and it can certainly be placed amount the most sensitive ones.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support of this work by Islamic Azad University, Omidieh branch.

REFERENCES

1. A. Ferrier, D. Garin and J.M. Crance, *J. Hosp. Infect*, **57**, 73 (2004).
2. Z. Holzbecher, L. Divis, M. Kraal, L. Suchaand and F. Valcil, Hand book of Organic Reagents in Inorganic Analysis. J. Wiley & Sons Co., N.Y. (1976).
3. N.N. Daoud, N.A. Dickinson and P. Gilbert, *Microbios*., **37**, 73 (1983).
4. J.J. Merianos, In ed.: S.S. Block, Disinfection, Sterilization and Preservation, Lea and Febiger, PA, pp. 225-255 (1991).
5. United States Pharmacopoeia 23/National Formulary 18, United States Pharmacopoeia Convention, Inc., Maryland, pp. 2218-2219 (1995).
6. B. Grillitsch, O. Gans, N. Kreuzinger, S. Scharf, M. Uhl and M. Fuerhacker, *Wat. Sci. Technol*., **54**, 111 (2006).
7. J.B. Lewis, *Chem. Eng. Sci*., **3**, 284 (1954).
8. J.D. Thornton, Science and Practice of Liquid-Liquid Extraction, Published in the U.S. by Oxford University Press, New York, edn. 1, pp. 2-6 (1992).
9. Z. Gh. Afshar and H. Parham, *Asian J. Chem*., **22**, 3009 (2010).
10. G.M. Ritcey and A.W. Ashbrook, Solvent Extraction: Principles and Applications to Process Metallurgy. Elsevier, Amsterdam, Part 1 (1984).
11. C. Hanson and R. Whewell, In eds.: J.A. Marinsky and Marcus, Solvent Extraction and Ion Exchange, Marcel Dekker, New York, edn. 3, p. 1 (1981).
12. H. Yamada and M. Tanaka, Advances in Inorgqnic and Radiochemistry, Academic Press, New York, edn. 29, p. 143 (1985).
13. N.M. Rice, *Hydrometallurgy*, **3**, 111 (1978).
14. G.Y. Marcovits and G.R. Choppin, ed.: Y. Marcus, Solvent Extraction, Marcle Dejjer, edn. 3, p. 51 (1973).
15. D.S. Flett and M.J. Jaycock, In ed.: Y. Marcus, Solvent Extraction, 9, Dekker, New York, edn. 3, p. 1 (1973).
16. J.A. Dean, Chemical Separation Methods, University of Tennessee, Van Nostrand Co., Ch. 3, pp. 19-54 (1969).
17. Y. Marcus and A.S. Kertes, Ion Exchang eand Extraction of Metal Complexes, Wiley Interscience Pub. Co., N.Y. (1969).
18. T. Brand and G. Ghersini, Extraction Chromatography, Elsevier Scientific Publishing Company, New York, edn. 1, p. 2 and 24 (1975).