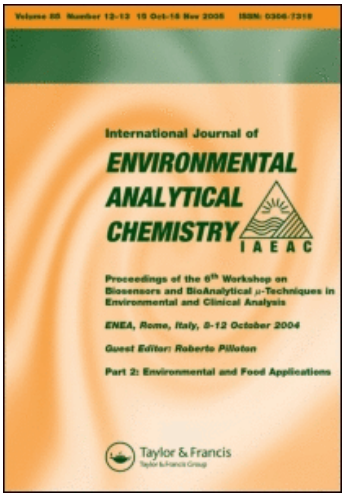

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Dialkyldimethylammonium Surfactants in Consumer Products and Aqueous Environmental Samples Using the Mixed Micelle-Based Methodology

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To cite this Article Borrego, Encarnación , Sicilia, Dolores , Rubio, Soledad and Pérez-Bendito, Dolores(1999) 'Determination of Dialkyldimethylammonium Surfactants in Consumer Products and Aqueous Environmental Samples Using the Mixed Micelle-Based Methodology', International Journal of Environmental Analytical Chemistry, 75: 1, 181 — 200
To link to this Article: DOI: 10.1080/03067319908047310
URL: http://dx.doi.org/10.1080/03067319908047310

Intern. J. Environ. Anal. Chem., Vol. 75(1-2), pp. 181-200
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DETERMINATION OF DIALKYLDIMETHYLAMMONIUM SURFACTANTS IN CONSUMER PRODUCTS AND AQUEOUS ENVIRONMENTAL SAMPLES USING THE MIXED MICELLE-BASED METHODOLOGY

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(Received 6 November 1998; In final form 23 April 1999)

The determination of dialkyldimethylammonium surfactants (DDAS) based on the measurement of the critical micelle concentration (CMC) of mixed sodium dodecylsulphate (SDS)-DDAS aggregates in a basic medium ([NaOH]=4.8×10^{-3} M) is proposed. The dye Coomassie Brilliant Blue G (CBBG) was used as a photometric probe for the rapid determination of CMCs. Formation of CBBG-DDAS and DDAS-SDS premicellar aggregates of well-defined stoichiometrics at cationic and anionic surfactant concentrations far below their CMCs is demonstrated. Increased SDS concentration in the titration medium results in the formation of DDAS-SDS mixed micelles. The strong interaction between the opposite charged head group of DDAS and SDS permits these cationic surfactants to be determined at the ng ml^{-1} level with a nearly uniform response for all the DDAS tested (12–18 alkyl carbons). The relative standard deviation for 1.10 μg ml^{-1} ditetradecyldimethylammonium bromide (DTDAB) was 1.5%. The mixed-micelle based methodology was applied to the determination of DDAS in softeners and aqueous environmental samples (river water and laundry effluents) with average recoveries ranged from 87.1 to 100.6 and from 96.3 to 104.0, respectively.

Keywords: Dialkyldimethylammonium surfactants; mixed-micelle based methodology; river water; laundry effluents

INTRODUCTION

Cationic surfactants, although representing only a small percentage (less than 10%) of the total European surfactant production, are broadly used in consumer products and industrial applications for their bacteriostatic, antistatic and textile

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softening properties. The most important cationic surfactant type is the formed by dialkyldimethylammonium surfactants (DDAS) with typically 12–18 alkyl carbons. They are used in fabric conditioning products and represent up to 70% of total cationic surfactants.

Determination of DDAS in aqueous solutions is routinely performed by a reduced number of photometric methods. The analytical basis of these non-specific determinations is the formation of solvent extractable compounds between the cationic surfactant and an intensely coloured specie. The most commonly used anionic reagent for this purpose is disulphine blue [1–3] whilst picric acid [4] and orange II [5] have also found some application. Atomic absorption spectroscopy has also been proposed for the determination of cationic surfactants [6–8]; an ion-pair between the cationic surfactant [6–7] or an anionic surfactant added in an accurately measured excess to the sample [8], and an opposite charged reagent containing a metal is extracted into an organic solvent. The metal (e.g. cobalt [6,7], copper [8]) present in the organic layer is measured by atomic absorption spectroscopy. Some of the methods based on absorbance [9] or atomic absorption measurements [10] have been automated using flow injection analysis (FIA). On the other hand, the two-phase ion-pair titrations employ potentiometric [11], visual [12] or photometric [13] end point detection in this field. The titration is performed using an anionic (e.g. sodium tetraphenylborate [11, 12], sodium dodecylbenzenesulphonate [13]) or a cationic (e.g. benzyldimethyltetradecylammonium [13]) titration agent in the direct and indirect titration method, respectively.

All the methods based on the formation of ion-pairs present some common drawbacks such as: 1) the sensitivity is not high enough for determining the low levels required in environmental monitoring of cationic surfactants (ng ml^{-1}), 2) poor selectivity since anionic interferences interact more strongly with cationic surfactants that does the anionic dye reagent and 3) recoveries which depend on the chain length of DDAS.

Although electrochemical techniques based on selective electrodes [14–15] have also been used for the determination of cationic surfactants, they present important disadvantages such as low sensitivity (μg ml^{-1}), electrode stability problems and non-linear responses.

In this paper we tried to solve some of these problems by using a new methodology [16] recently developed in our laboratory for the determination of amphiphilic substances. This methodology is based on measurements of the critical micelle concentration (CMC) of binary mixtures of amphiphilic substances (one of which is the analyte) and it has proved useful for the determination of alkyl sulphates [17], monoalkyl quaternary ammonium salts [18–19], alkoxylated alcohols [16] and polysorbates [20]. In this context, anionic-cationic surfactant

mixtures are a specially intriguing subset of surfactants inasmuch as the opposite charges give rise to unusual solution aggregates of "pseudo-nonionic" character [21]. These systems exhibit strong synergism relative to the properties (e.g. CMC) of their individual compounds, and this behaviour permits the sensitive determination of surfactants [19]. For this reason, the anionic surfactant sodium dodecylsulphate was selected for the formation of binary mixtures with DDAS. The applicability of the proposed method for the determination of the cationic surfactants studied in consumer products (softeners) and aqueous environmental samples (river water and laundry effluents) was evaluated.

EXPERIMENTAL

Chemicals

Commercially available highest grade chemicals were used throughout, without further purification. A 6.6×10^{-5} M aqueous solution of Coomassie Brilliant Blue G (CBBG, Sigma) was made by dissolving 0.0626 g of the reagent in 1 l of distilled water with sonication for 15 min. Aqueous solutions of sodium chloride (5.0 M), sodium hydroxide (8.0×10^{-2} M) and sodium dodecyl sulphate (0.75 g l^{-1}, Aldrich) were also made. Solutions of the dialkyldimethylammonium surfactants (DDAS) didodecyldimethylammonium bromide (DDDAB, 10 mg l^{-1}, Fluka), ditetradecyldimethylammonium bromide (DTDAB, 10 mg l^{-1}, Fluka), dihexadecyldimethylammonium bromide (DHDAB, 1.0 mg l^{-1}, Aldrich) and dioctadecyldimethylammonium bromide (DODAB, 0.5 mg l^{-1}, Fluka) were prepared in distilled water. These stock solutions remained stable for at least one week. The anion exchange resin Dowex 2X8 (chloride form, 50–100 mesh, exchange capacity= 3.5 meq g^{-1}) was obtained from Sigma. Solvents (chloroform and methanol) and alumina "B" were purchased from Panreac.

Apparatus

The equipment used consisted of a Mettler DL 40 Memotitrator furnished with a 10 ml autoburette, a fan stirrer, a titration vessel and a Mettler GA 14 recorder. The detection unit was a Metrohm 662 spectrophotometer equipped with an immersion probe (1 cm pathlength).

Samples collection and preservation

Samples from laundry effluent (Maria Auxiliadora, Córdoba, Spain) and the Guadalquivir River Córdoba, Spain) were collected. All environmental samples

were preserved with 1% formaldehyde and 10 μg ml^{-1} of Triton X-100 to reduce adsorption of the cationic surfactants to the inside of the polyethylene storage containers. They were stored at 4°C prior to preparation. The softeners, Pryca, Quanto and Lenor, manufactured by Tendesa S.A. (Madrid, Spain), Benckser España S.A. (Barcelona, Spain) and Procter-Gamble España S.A. (Madrid, Spain), respectively were analyzed as purchased.

Preparation of anion-exchange columns and alumina cartridges

Anion-exchange columns: The Dowex 2X8 anion-exchange resin (3.0 g) was rinsed with two 20-ml portions of methanol with stirring for 30 min with each of such portions. A plug of glass wool was placed in the bottom of an ion-exchange column (10-mm i.d.) and was filled with the preconditioned resin (100-mm long).

Alumina "B" cartridges: Alumina "B" (3.0 g) was baked at 450 °C for 1 h and added to an cartridge (10-mm.d., 50-mm long). The alumina "B" cartridge was rinsed by passing 30 ml of chloroform at a rate of less than 3 ml min^{-1}.

Isolation of cationic surfactants

Cationic surfactants were isolated from other anionic or nonionic surfactants present in samples (laundry effluent, river water or softeners) by using the following procedure (Figure 1): 1) A volume of sample containing 25–500 μg of total DDAS was evaporated to dryness at reduced pressure. The volume of the sample should preferably not exceed 200 ml. 2) The cationic surfactants were extracted from the dried residue with two 20 ml-portions of boiling methanol. The whole methanolic extract was passed through the prepared anionic-exchange Dowex 2X8 column at a rate of less than 1 ml min^{-1} and the effluent was collected into a round bottom flask. Then, the anionic exchange column was washed with 10 ml of methanol in order to ensure quantitative recovery of the DDAS. 3) The combined effluents were evaporated to dryness at reduced pressure and the dried residue was redissolved in 90 ml of chloroform. The chloroform extract was passed through the prepared alumina "B" cartridge at a rate of less than 3 ml min^{-1} and the cartridge was rinsed with 30 ml of chloroform. 4) The cationic surfactants were eluted from the alumina "B" cartridge with 10 ml of chloroform/methanol (3:1) and the eluate was collected into a round bottom flask. 5) This eluate was evaporated to dryness at reduced pressure and the dried residue was redissolved in 25 ml of distilled water. An aliquot (between 5 and 20 ml) of this aqueous sample solution was analyzed as described afterwards.

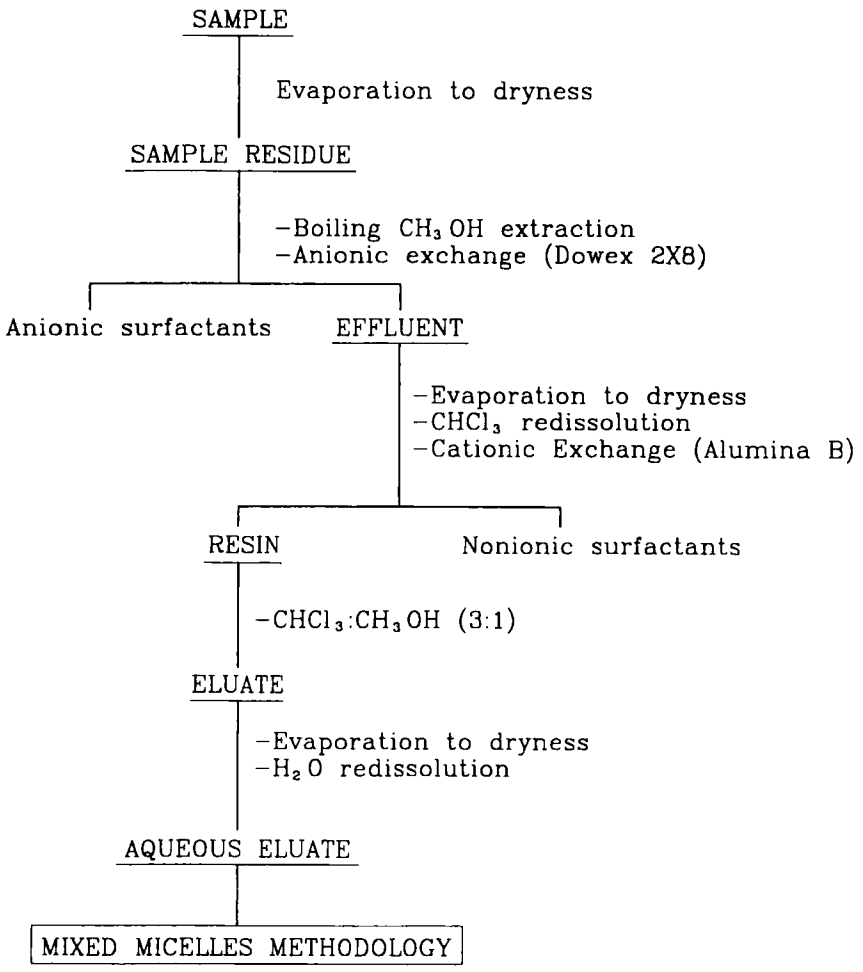


FIGURE 1 Schematic procedure for the isolation of cationic surfactants

Procedure for the determination of cationic surfactants

Volumes of 4 ml of 6.6×10^{-5} M CBBG solution, 3 ml of 8.0×10^{-2} M sodium hydroxide, 12,5 ml of 4 M sodium chloride, and an aliquot of standard, or treated sample solution of DDAS were placed in a 50 ml standard flask and distilled water was added to the mark. This solution was placed in a 100 ml titration vessel and titrated with 0.75 g l^{-1} SDS from the burette at a rate of 4 ml min^{-1}. The stirring rate was set at 250 rpm. Titration curves were obtained by recording the absorbance at 600 nm as a function of the titrant volume. The end-point was

determined graphically from the intercept of the straight lines extrapolated before and after the equivalence point. The concentration of DDAS was determined from the following expression [16]:

$$1 - \frac{C_2^M}{f_2 C_2} = \frac{1}{f_1 C_1} C_1^M \quad (1)$$

By plotting the parameter $1\text{-}C_2^M/C_2$ as a function of the concentration of cationic surfactant (C_1^M), linear calibrations were obtained which indicates that the activity coefficient of the analyte (f_1) in the mixed micelle remained unchanged and that of the titrant (f_2) was unity over the range of C_1^M values considered. C_1^M and C_2^M in eqn. (1) denote the concentrations of monomeric DDAS and SDS, respectively, and C_1 and C_2 the CMC of pure DDAS and SDS, respectively. The sum of C_1^M and C_2^M corresponds to the critical micelle concentration of the DDAS-SDS mixed micelles.

The parameters needed to construct the calibration graphs were extracted from titration curves. Thus, the amount of surfactant used in the titration, expressed as a molar concentration, corresponded to C_2^M and the threshold value for aggregation of SDS single micelles (C_2) was determined from the surfactant consumed in the titration of a blank solution (without DDAS).

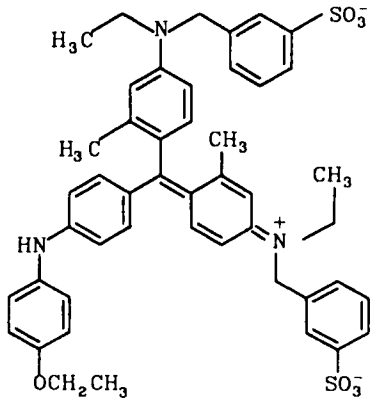
RESULTS AND DISCUSSION

Study of CBBG-DDAS interactions

The dye CBBG has been frequently used for rapid CMC determinations [22]. Its structure and those corresponding to the DDAS studied are depicted in Figure 2. Since dye and DDAS bear charges of different sign their interaction will be governed by both electrostatic and hydrophobic forces. Evidence of the strong interaction between CBBG and DDAS in the basic titration medium (4.8×10^{-3} M NaOH) could be obtained from the DDAS-induced CBBG spectral changes. Concentrations of DTDAB, which was the DDAS used as a model, far below its CMC (lower than about two orders of magnitude) caused a considerable decrease in the absorbance of CBBG at the maximum absorption peak (compare curves 3 and 4 in Figure 3). In a neutral medium, no evidence of interaction between CBBG and DTDAB was observed (compare curves 1 and 2 in Figure 3).

In the basic titration medium, the possibility of a well-defined stoichiometry of DTDAB to CBBG was investigated by using the mole-ratio method. Experiments were carried out by mixing increasing DTDAB concentrations, far below the CMC and within the range of analytical interest (0–4.0×10^{-6} M) and a con-

A



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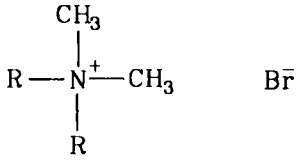

DDAS	R
DDDAB	$-(CH_2)_{11}-CH_3$
DTDAB	$-(CH_2)_{13}-CH_3$
DHDAB	$-(CH_2)_{15}-CH_3$
DODAB	$-(CH_2)_{17}-CH_3$

FIGURE 2 Structures of (A) CBBG and (B) DDAS

stant concentration of dye (5.3×10^{-6} M). Figure 4 shows the variation of the absorbance at 590 nm as a function of the DTDAB/CBBG ratio. The broken line obtained suggested the formation of DTDAB : CBBG aggregates of different stoichiometry (between 1:25 to 1:2) in proportion to the DTDAB concentration increased. Based on these results and taking into account that CBBG has been reported to form aggregates in water [18], we can conclude that dye aggregates act as a nucleus from which monomers of DTDAB gradually associate.

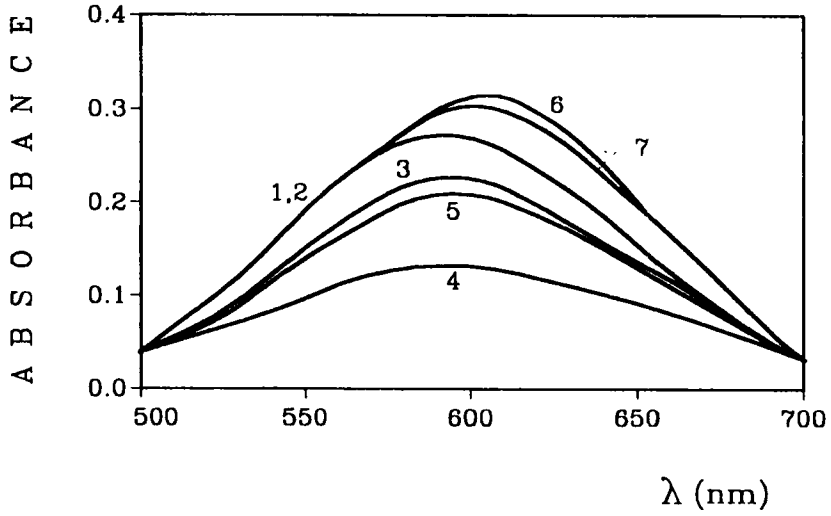

FIGURE 3 Spectra for Coomassie Brilliant Blue G (5.3×10^{-6} M) in a neutral (1, 2) and basic medium ([NaOH] = 4.8×10^{-3}M) (3–7), in the absence of surfactant (1, 3) and the presence of DTDAB (2.1 μg ml^{-1}) (2, 4), DTDAB (2.1 μg ml^{-1}) and SDS (18.4 μg ml^{-1}) (5), SDS (1.15 g l^{-1}) (6), and DTDAB-SDS (2.1 μg ml^{-1} and 1.15 g l^{-1} (7), respectively)

Study of CBBG-DDAS-SDS interactions

In the basic titration medium (4.8×10^{-3} M NaOH) addition of SDS, at concentrations far below its CMC (lower than about three orders of magnitude), to the DTDAB-CBBG system caused further modifications in the spectral features of the dye (Figure 3, compare curves 4 and 5). Therefore, the possibility of a well defined stoichiometry of SDS to DTDAB was also investigated. The concentrations of dye and DTDAB were constant at 5.3×10^{-5} M and 4.0×10^{-6} M, whereas that of SDS was changed between 0 and 3.0×10^{-4}M. A gradual increase in the absorbance at 590 nm as a function of the SDS/DTDAB molar ratio was observed (Figure 4B), which could be explained on the basis of the formation of mixed SDS-DTDAB premicellar aggregates of different stoichiometry (between 1:1 and 9:1). At SDS/DTDAB molar ratios between 1:9 and 1:75 (results no shown) no significant increase of the absorbance at 590 nm was observed.

Formation of single SDS micelles in the titration medium caused a bathochromic shift in the maximum absorption of CBBG from 590 to 605 nm and a hyperchromic effect at 605 nm (curve 6 in Figure 3). Addition of DDAS, at the micromolar level, to the SDS-CBBG system caused further modifications in the spectral features of CBBG (compare curves 6 and 7 in Figure 3) due to the formation of DDAS-SDS mixed micelles.

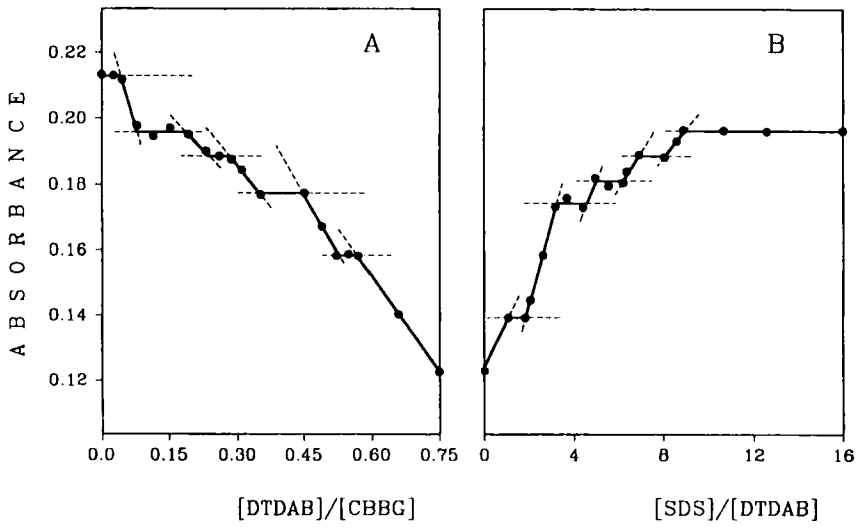

FIGURE 4 Variation of the absorbance of Coomassie Brilliant Blue G (5.3×10^{-6} M) at 590 nm as a function of (A) DTDAB/CBBG and (B) SDS/DTDAB molar ratios. (B) [DTDAB] = 4.0×10^{-6} M

Figure 5 shows the experimental curves obtained at 605 nm by titration of 4.0×10^{-6} M DTDAB, with SDS at different pH values. Initial absorbance was set at 0.0. In the basic medium provided by NaOH, titration curves showed two different regions which corresponded to the formation of mixed DTDAB-SDS premicellar and micellar aggregates, respectively. Thus, addition of very low volumes of SDS resulted in a sharp increase in the absorbance recorded at 605 nm until a maximum value was reached. This maximum increased as a function of the sodium hydroxide concentration up to about 4.0×10^{-3} M, then its value was kept constant for higher hydroxide concentrations. The absorbance increment was found to be proportional to the DTDAB concentration (Figure 9). Addition of more SDS to the titration medium provided typical titration curves, the end-point of which was also dependent on the pH of the medium (Figure 5).

In conclusion, CBBG interacts strongly with DTDAB in a basic medium which induces the formation of cationic premicellar aggregates. The same behaviour has been observed for all DDAS studied The anionic surfactant SDS is gradually incorporated into the premicellar aggregates proportionally as its concentration is increased to form mixed DDAS-SDS premicellar aggregates. At SDS concentrations high enough, mixed DDAS-SDS micelles are formed that solubilize CBBG.

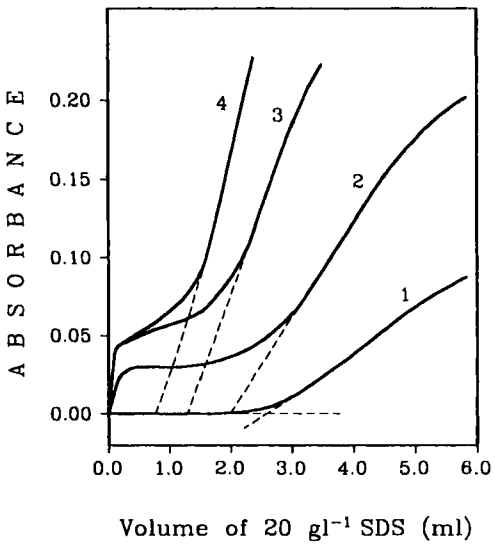

FIGURE 5 Variation of the absorbance of Coomassie Brilliant Blue G (5.3×10^{-6} M) at 605 nm as a function of the volume of titrant (20 g l^{-1}) SDS added to a titration vessel containing DTDAB (1.09 μg ml^{-1}) in a neutral (curve 1) and basic (curves 2–4) medium. [NaOH]: (curve 2) 1.6×10^{-3} M, (curve 3) 4.0×10^{-3} M and (curve 4) 1.3×10^{-2} M

Optimization of the experimental conditions for the determination of DDAS

The effect of different variables (hydrogen ion and CBBG concentration, ionic strength and dielectric constant) on C_2, C_2^M and the measurement parameter $1-(C_2^M/C_2)$ was investigated. The aim was two-fold: (1) to find the optimal experimental conditions for determining DDAS (e.g. the best possible sensitivity in their determination and the highest possible precision in the determination of the end-point of titration curves) and (2) to compare the behaviour of DDAS-SDS aggregates in both a neutral and basic medium.

The effect of altering the hydrogen ion concentration on the micellization of DDAS-SDS aggregates and on the measurement parameter was studied by adding sodium hydroxide (Figure 6B) and sulphuric acid (Figure 6A) in the titration medium. Sulphuric acid was found to affect the spectral features of CBBG in both aqueous and micellar media, so in this medium, titrations were performed at 650 nm in order to obtain adequate titration curves. Micellization of both single SDS (C_2) and mixed DDAS-SDS micelles (C_2^M) was markedly favoured by addition of acids and bases to the titration medium (Figure 6A2 and 6B2, respectively). However, different effects on the measurement parameter were observed.

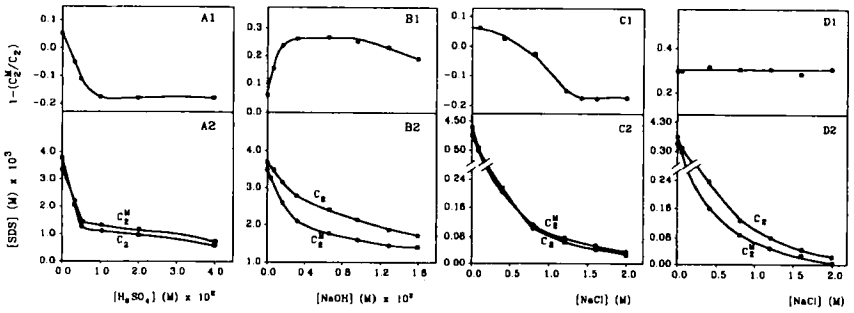

FIGURE 6 Influence of the (A,B) hydrogen ion concentration and (C,D) ionic strength on (1) the measurement parameter and (2) C_2 and C_2^M, studied by adding (A) H_2SO_4, (B) NaOH and (C,D) NaCl in a (C) neutral and (D) basic medium ([NaOH] = 4.8×10^{-3}. M). [CBBG] = 5.3×10^{-6} M; [DTDAB] = 1.10 μg ml^{-1}; λ = (A) 650 nm and (B, C, D) 605 nm

Addition of sulphuric acid to the titration medium resulted in a decrease in the measurement parameter, which reached negative values at acid concentrations higher than 1.5×10^{-3} M (Figure 6A1). This effect was similar to that provided by electrolytes in a neutral medium (Figure 6C1). On the other hand, the measurement parameter increased as a function of the sodium hydroxide concentration up to about 3.0×10^{-3} M (Figure 6B1). The maximum value reached, which was about 5-fold higher than that obtained in a neutral medium remained constant in the sodium hydroxide concentration range between about 3.0×10^{-3} M and 1.0×10^{-2}M. This behaviour cannot be only ascribed to an electrolytic effect but to the dependence of the micellization process with pH.

The electrolyte effect on the micellization of both single and mixed aggregates, and also on the measurement parameter, was examined by using sodium chloride concentrations between 0 and 2.0 M. Figures 6C and 6D show the results obtained in both a neutral and a basic ([NaOH]=4.8×10^{-3} M) medium, respectively. Addition of electrolyte favoured the formation of both single and mixed micellar aggregates of SDS whatever the pH of the titration medium (Figures 6C2 and 6D2), mainly owing to the decrease in the thickness of the ionic atmosphere surrounding the SDS anionic head groups and the consequent decreased electrical repulsion between them in the aggregate. However, the variation of the measurement parameter as a function of the electrolyte concentration was strongly dependent on the pH of the titration medium. In a neutral medium, the measurement parameter decreased on addition of sodium chloride at concentrations between 0.2 and 1.4 M, reaching negative values at salt concentrations higher than 0.6 M (Figure 6C1). On the contrary, no effect on the measurement parameter over the sodium chloride concentration range tested was observed in the basic titration medium (Figure 6D1).

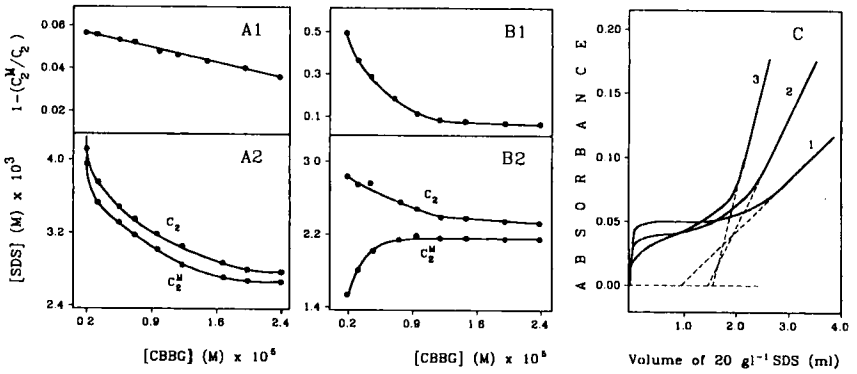

FIGURE 7 (A, B) Influence of the Coomassie Brilliant Blue G concentration on (1) the measurement parameter and (2) C_2 and C_2^M in a (A) neutral and (B) basic medium ([NaOH] = 4.8×10^{-3} M). (C) Variation of the absorbance of Coomassie Brilliant Blue G at 605 nm as a function of the volume of titrant (20 g l^{-1}) SDS added to a titration vessel containing DTDAB (1.10 μg ml^{-1}. [CBBG]: (1) 2.6×10^{-6} M, (2) 5.3×10^{-6} M and (3) 1.1×10^{-5} M. [NaOH]= 4.8×10^{-3} M; λ = 605 nm

Analytically, a basic medium ([NaOH] = 4.8×10^{-3} M) and an ionic strength of 1 M adjusted with sodium chloride is recommended for determining DDAS in real samples on the basis of the increased sensitivity and precision achieved, as well as the unlikely dependence of the signal on the electrolyte content in the analyzed sample.

Increasing concentrations of CBBG throughout the range studied (0.2–2.4)$\times10^{-5}$ M resulted in a decrease of the CMC of single SDS micelles (C_2) in both a neutral and a basic ([NaOH]=4.8×10^{-3} M) medium (Figures 7A2 and 7B2, respectively). Incorporation of the dye to SDS molecules decreased the work required for micellization by decreasing the mutual repulsion of the anionic surfactant heads in the micelle. The effect of CBBG concentration on the formation of mixed DDAS-SDS aggregates in a neutral medium was similar to that observed on single SDS micelles (Figure 7A2, C_2^M). However in a basic medium this effect was quite different; the C_2^M value increased as a function of the CBBG concentration up to 8.0×10^{-6} M (Figure 7B2) due to competition between CBBG and SDS to interact with DDAS (Figure 7C shows through the absorbance increment at the initio of the titration how the formation of mixed DDAS-SDS premicellar aggregates was disfavoured by increasing the CBBG concentration). A decreased measurement parameter as a function of the dye concentration was observed (Figures 7A1 and 7B1), this effect being more pronounced in a basic medium. Taking into account these results and that CBBG concentrations below about 5.0×10^{-6}M provided inadvisable since the absorb-

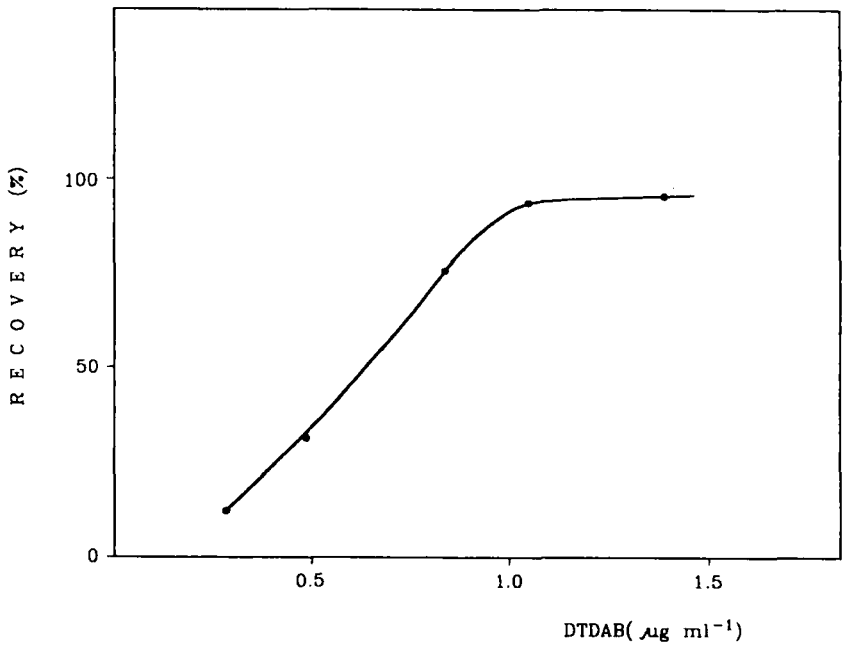

FIGURE 8 Recovery of DTDAB achieved in the water evaporation process as a function of the cationic surfactant concentration. Initial aqueous sample volume = 200 ml

ance increase as a function of the concentration of SDS was very small and detracted from precision in the determination of the titration endpoint, a dye concentration of 5.3×10^{-6} M was selected as a photometric probe.

The effect of organic additives on the formation of both single and mixed micelles was studied by addition of methanol and formaldehyde, at concentrations up to 20%. The alcohol was found not to affect the formation of aggregates in proportions below about 5%. Higher contents of this solvent disfavoured micellization. On the other hand, micelles were no formed in the presence of formaldehyde at concentrations higher than 8%. Lower percentages of this solvent disfavoured micellization. Organic additives can increase the CMC of surfactants by disruption of the water structure, thus increasing the solubility of the monomeric form of the surfactant or decreasing the dielectric constant. No effect on the measurement parameter in the presence of methanol was observed in the range of concentrations tested. However, it decreased as a function of the formaldehyde concentration up to about 2 % and then it kept constant.

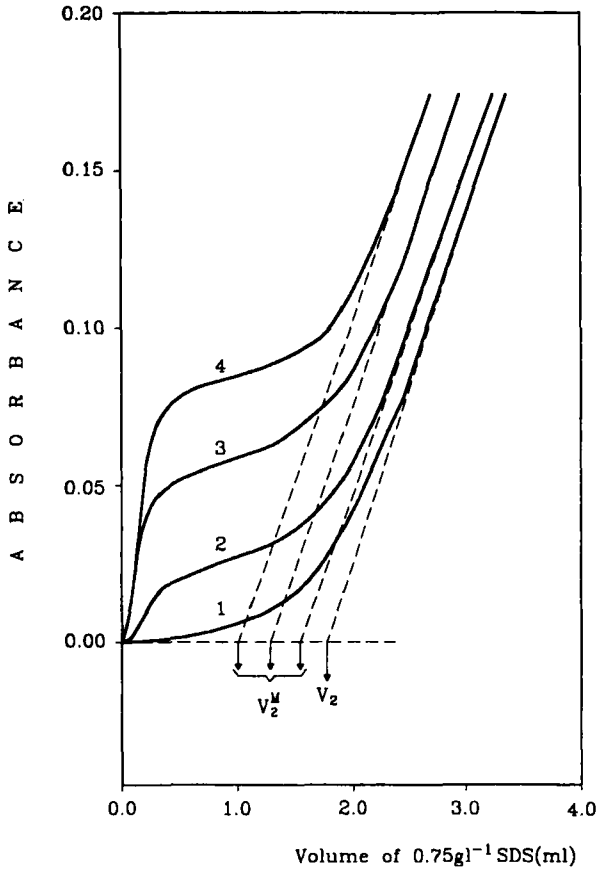

FIGURE 9 Variation of the absorbance of Coomassie Brilliant Blue G (5.3×10^{-6} M) at 605 nm as a function of the volume of titrant (0.75 g l^{-1}) SDS added to a titration vessel containing no cationic (curve 1) surfactant or DTDAB concentrations of: (curve 2) 0.44, (curve 3) 0.88 and (curve 4) 1.32 μg ml^{-1}. [NaOH] = 4.8×10^{-3} M; [NaCl] = 1.0 M

Optimization of the DDAS isolation process

Cationic surfactants can be extracted from aqueous samples by stripping them with nitrogen [23], the main drawback of this methodology being that molecules adsorbed on suspended particles are not isolated. An more efficient extraction method has been suggested by Osburn [3], which includes evaporation of the aqueous sample to dryness and extraction by methanolic acid. Extraction from the dried residue with boiling methanol has also been proposed [2]. Separation of the cationic surfactants from other possible interferents in the sample has been

performed in an alumina B cartridge using a mixture of methanol and chloroform as eluent [24, 25]. For isolation from anionic surfactants, anionic resins have been employed [2, 3].

Different studies were carried out in order to design a procedure for the separation of cationic surfactants from anionic and nonionic surfactants in aqueous environmental samples. These studies were focused in selecting the best experimental conditions for each of the different steps involved in the isolation process (Figure 1).

Evaporation to dryness of water samples containing different amounts of DTDAB proved that this surfactant is unstable at concentrations lower than about 1 $\mu g\ ml^{-1}$. The same behaviour was observed for all DDAS studied. Recoveries of DTDAB decreased in proportion to the cationic surfactant did (Figure 8). In order to avoid looses of DDAS during the water evaporation process, different procedures described in the literature [2–3] for preservation of cationic surfactants in aqueous samples were evaluated. Surfactants of different nature: alkyl benzenesulphonate (sodium dodecyl benzenesulphonic acid), alkyl sulphate (sodium hexadecyl sulphate) and alkylphenol ethoxylates (Triton N-60) at different surfactant/DTDAB molar ratios (3:1 for anionic and 20:1 for nonionic surfactants) were added to a 200 ml-aqueous sample containing 0.4 $\mu g\ ml^{-1}$ of DTDAB before starting the water evaporation process. Recoveries of DTDAB were determined by using the scheme depicted in Figure 1. The surfactants tested proved to be unable to preserve DDAS at concentration levels lower than 1 $\mu g\ ml^{-1}$); no significant improvement in the recoveries of DTDAB from aqueous samples was obtained in the presence of the anionic and nonionic surfactants tested.

Separation of cationic from anionic surfactant was performed in a Dowex 2X8 anionic-exchange resin (Figure 1). It was checked that anionic surfactant at 3:1 anionic surfactant/DDAS molar ratios was completely removed from aqueous samples containing 150 μg of DTDAB.

Different cationic-exchange and reverse phase materials for the separation of DDAS from nonionic surfactants were tested. Results obtained are summarized in Table I. Cationic resins such as Amberlite CG-50 and Amberlyst 15 were found not to retain completely DTDAB under the experimental conditions tested. Other cationic resins (e.g. Amberlite CG-120) completely retained DTDAB but its elution was impossible. Hydrochloric acid demonstrated to be unable to elute the cationic surfactant from Amberlite CG-120 and when BaCl or $Fe(NO_3)_3$ solutions were used as eluent, precipitation occurred in the basic titration medium. In order to avoid precipitation different complex agents were tested (e.g. EDTA, fluoride and cyanide). Although in the presence of EDTA or fluoride no precipitation occurred in the titration medium, no response for DTDAB using

the mixed micelle-based methodology was obtained. When precipitate was removed before titration, DTDAB was not detected. Using reverse phase extraction columns of C_8 retention of 100% DTDAB was achieved, however no elution neither CH_3OH nor $CHCl_3$ was provided. Finally, using alumina B cartridges the best results were obtained; DTDAB was completely retained and a high percentage of the cationic surfactant (92.6%) was eluted by $CHCl_3/CH_3OH$ 1:3.

It was checked that the isolation of cationic from anionic and nonionic surfactants required both anionic and cationic exchange in the order specified in Figure 1. Thus, DDAS were not retained in the alumina B cartridge in the presence of anionic surfactants.

Recovery of DDAS from spiked aqueous samples, after applying the complete isolation procedure developed (Figure 1), was evaluated to be about 85 %. Therefore, the determination of DDAs in consumer products and aqueous environmental samples was performed by taking into account this recovery factor.

Calibration

Calibration graphs for DDAS were run by plotting $1\text{-}C_2^M/C_2$ versus the cationic surfactant concentration (C_1^M). The DDAS selected for this purpose were those used in consumer products and industrial applications (DDDAB, DTDAB, DHDAB and DODAB). Figure 9 shows titration curves obtained under the optimized experimental conditions ([NaOH]=4.8×10^{-3} M, NaCl]= 1 M) in the absence (curve 1) and presence of different DTDAB concentrations (curves 2–4). Table II compares the figures of merit of the calibration graphs obtained for each of cationic surfactants tested. Linear calibration curves were obtained in all cases [standard errors of the estimate and correlation coefficients varied over the ranges $(0.4\text{–}1.0)\times10^{-2}$ and 0.992–0.9996, respectively]; therefore, parameters f_2 and f_1 remained constant over these linear concentration ranges. Also, intercept values were not significantly different from zero, so f_2 (the activity coefficient for SDS in the mixed micelles) should be approximately unity.

As can be inferred from the slopes of the calibration curves obtained (Table II), a nearly uniform response was exhibited by the DDAS examined. The greater DDAS concentration in the linear concentration range was fixed for the solubility in water of each cationic surfactant; thus, the narrowest linear concentration range was obtained for the most hydrophobic surfactant (DODAB).

The precision of the proposed method, expressed as relative standard deviation, was 1.5% (n=11) at a DTDAB concentration of 1.10 $\mu g\ ml^{-1}$.

TABLE I Materials tested for the separation of DDAS from nonionic surfactant

Material for separation of DDAS	*Pretreatment of the material for separation of DDAS*	*[i]% DTDAB retained*	*Eluent*	*% DTDAB eluted*	*Observations*
[a]Amberlite CG-50	[f]CH_3OH	1.9	12 M HCl/CH_3OH (3:75)	0	
	[f]0.2M NaOH, H_2O to pH=8.0	52.7	1M HCl	81.4	
			5M HCl		Complete degradation of DTDAB
[b]Amberlite CG-120	[f]CH_3OH	0.0			
	[f]H_2O	100.0	1M HCl	0	
			1M BaCl	—	Precipitate formed in the basic titration medium
			1M $Fe(NO_3)_3$	—	
[c]Amberlyst 15	[f]CH_3OH	75.5	12 M HCl/CH_3OH (3:50)	24.8	
[d]C_8 column	[g]CH_3OH, H_2O	100.0	CH_3OH	0	
			$CHCl_3$	0	
[e]Alumina B	Baked at 450°C [h]$CHCl_3$	100.0	$CHCl_3$/CH_3OH (3:1)	92.6	

a. Active group: – COOH; H^+-form; 100–200 mesh; 10 meq/g; 0.2 g. [b]Active group: – SO_3H; Na^+-form; 100–200 mesh; 4.4 meq/g; 0.2 g. [c]Active group: – SO_3H; H^+-form; 100–200 mesh; 4.7 meq/g; 0.5 g. [d]0.5 g of C_8. [e]3.0 g. [f]resins were rinsed with the adequate solvent for 1 h with magnetic stirring and a column was filled with pretreated resins. [g]C_8 columns were rinsed with 10 ml of CH_3OH and 10 ml of bidistilled water. [h]alumina B cartridges were rinsed with 30 ml of $CHCl_3$. [i] DTDAB was solubilized in the solvent used in the pretreatment of the material and passed through the corresponding column at a rate of less than 1 ml min^{-1}. Amount of DTDAB: 55 μg

TABLE II Analytical figures of merit of the proposed method for the determination of DDAS

DDAS	*Linear concentration range (mg l^{-1})*	*Intercept ± s.d.*	*Slope ± s.d. (mg^{-1} l)*	r^a	SEE^b ($\times 10^2$)
DDDAB	0.1–1.8	$(9 \pm 3) \times 10^{-3}$	0.274 ± 0.004	0.9995	0.5
DTDAB	0.1–1.8	$-(4 \pm 3) \times 10^{-3}$	0.266 ± 0.003	0.9996	0.5
DHDAB	0.1–0.6	$(2 \pm 7) \times 10^{-3}$	0.26 ± 0.02	0.992	1.0
DODAB	0.1–0.3	$(0 \pm 3) \times 10^{-3}$	0.27 ± 0.02	0.992	0.4

a. Correlation coefficient, n = 8; [b]standard error of the estimate
b. [NaOH] = 4.8×10^{-3}M, [NaCl] = 1.0 M, $C_2 = (8.7 \pm 0.2) \times 10^{-5}$ M

Determination of DDAS in consumer products and aqueous environmental samples

In order to test the applicability of the proposed methodology for the determination of DDAS in consumer products, it was used for the analysis of these cationic surfactants in different commercial softeners. Results obtained using the mixed micelle-based methodology (Table III) were consistent with those provided by the disulphine blue standard method [1]. Recovery studies from these commercial products were performed by spiking different softeners with 1.0 and 2.0 mg/g DTDAB. Results obtained are also shown in Table III. It can be seen that the recoveries found were highly satisfactory.

TABLE III Recovery of DTDAB from softeners

Trade name	*Concentration (mg/g)*		*Recovery (%)*
	Added	*[a]Found [b](s.d.)*	
Pryca		3.2 (0.19)	
	1.0	3.89 (0.08)	92.0
	2.0	4.7 (0.10)	90.4
Quanto		2.26 (0.09)	
	1.0	2.84 (0.08)	87.1
	2.0	3.9 (0.22)	91.5
Lenor		4.07 (0.15)	
	1.0	4.8 (0.17)	94.7
	2.0	6.1 (0.16)	100.5

a. Mean of three independent determinations.
b. standard deviation.

The ability of the mixed micelle-based methodology to determine DDAS in aqueous environmental samples was confirmed by spiking different cationic surfactants-free water samples (river water and laundry effluents) with DTDAB concentrations comprised between 1.3 and 15.0 mg/g. The average recoveries for the water samples ranged from 96.3 to 104.0 (see Table IV), which testifies the fitness of the proposed method to its intended purpose.

TABLE IV Recovery of DTDAB from effluents

Sample	*Concentration (mg/g)*		*Recovery (%)*
	Added	*[a]Found [b](s.d.)*	
River Water	3.0	2.9 (0.18)	96.7
	5.0	5.2 (0.23)	104.0
	7.0	7.1 (0.16)	101.4
Laundry effluent	1.3	1.3 (0.08)	100.0
	3.0	3.1 (0.19)	103.3
	5.0	4.91 (0.06)	98.2
	7.0	7.1 (0.18)	101.4
	10.4	10.2 (0.2)	98.1
	12.0	12.1 (0.16)	100.8
	15.0	14.8 (0.25)	98.7

a. Mean of three independent determinations.
b. standard deviation.

CONCLUSIONS

The mixed micelle-based methodology has been demonstrated to offer important advantages over the widely used non-specific analytical methods based on ion-pairs: 1) higher sensitivity (the strong interaction between the opposite charged head groups of the DDAS and SDS, used as titrant, permits the determination of these cationic surfactants at the ng ml^{-1} level. Sensitivity afforded by methods based on ion-pairs is at the $\mu g\ ml^{-1}$ level), 2) responses that are independent of the alkyl chain length, 3) rapidity (titration curves can be recorded in a few seconds) and 4) highly experimental simplicity. This method has been successfully applied to the determination of DDAS in consumer products (softeners) and aqueous environmental samples (river water and laundry effluents).

Further studies are required in order to avoid losses of DDAS during treatment; specially at low DDAS concentrations (lower than 1 $\mu g\ ml^{-1}$).

Acknowledgements

The authors gratefully acknowledge financial support from Spain's CICyT (Project PB-96–0984).

References

1. H.K. Biswas and B.M. Mandal, *Anal. Chem.*, **44**, 1636–1640 (1972).
2. J. Waters and W. Kupfer, *Anal. Chim. Acta*, **85**, 241–251 (1976).
3. Q.W. Osburn, *J. Am. Oil Chem. Soc.*, **59**, 453–457 (1982).
4. I. Sheiham and T.A. Pinfold, *Analyst*, **94**, 387–388 (1969).
5. G.V. Scott, *Anal. Chem.*, **40**, 768–773 (1968).
6. A. Le Bihan and J. Courtot-Coupez, *Analusis*, **4**, 58–64 (1976).
7. S. Chattaraj and A.K. Das, *Anal. Lett.*, **25**, 2355–2366 (1992).
8. M. Mauzac, F. Guérard, J. Mathieu and J. Laroch, *Analusis*, **4**, 236–245 (1976).
9. J. Kawase, *Anal. Chem.*, **52**, 2124–2127 (1980).
10. P. Martínez-Jiménez, M. Gallego and M. Valcárcel, *Anal. Chim. Acta*, **215**, 233–240 (1988).
11. M. Tsubouchi, H. Mitsushio and N. Yamsaki, *Anal. Chem.*, **53**, 1957–1959 (1981).
12. S. Motomizu, Y.H. Gao, K. Uemura and S. Ishihara, *Analyst*, **119**, 473–477 (1994).
13. S. Pinzauti and E. La Porta, *Analyst*, **102**, 938–942 (1977).
14. L. Campanella, L. Aiello, C. Colapicchioni and M. Tomassetti, *Analusis*, **24**, 387–391 (1996).
15. L. Campanella, L. Aiello, C. Colapicchioni and M. Tomassetti, *Anal. Lett.*, **30**, 1611–1629 (1997).
16. D. Sicilia, S. Rubio and D. Pérez-Bendito, *Anal. Chem.*, **67**, 1872–1880 (1995).
17. I. Casero, D. Sicilia, S. Rubio and D. Pérez-Bendito, *Anal. Chim. Acta*, **345**, 75–86 (1997).
18. I. Casero, D. Sicilia, S. Rubio and D. Pérez-Bendito, *Talanta*, **45**, 167–180 (1997).
19. E. Borrego, D. Sicilia, S. Rubio and D. Pérez-Bendito, *Anal. Chim. Acta*, 384, 105-115 (1999).
20. E. Borrego, D. Sicilia, S. Rubio and D. Pérez-Bendito, *Anal. Chim. Acta*, 384, 175-183 (1999).
21. A. Mehreteab and F.J. Loprest, *J. Colloid Interface Sci.*, **125**, 602–609 (1988).
22. K.S. Rosenthal and F. Koussaie, *Anal. Chem.*, **55**, 1115–1117 (1983).
23. R. Wickbold, *Tenside Detergents*, **8**, 61–63 (1971).
24. J.R. Simms, T. Keough, S. R. Ward, B.L. Moore and M.M. Bandurraga, *Anal. Chem.*, **60**, 2613–2620 (1988).
25. K. Levawn, M. Emmrich and S. Behnert, *Fresenius J. Anal. Chem.*, **346**, 732–737 (1993).