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Determination of zwitterionic and cationic surfactants by high-performance liquid chromatography with chemiluminescenscent nitrogen detection

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Abstract

The use of chemiluminescent nitrogen specific detection (CLND) combined with an HPLC separation allows for the identification and quantification of cationic and zwitterionic surfactants. The CLND provides equimolar responses, based on the amount of nitrogen within any compound. This allows for the detection of any nitrogen containing surfactant. Reversed-phase separation methods using cyano columns are developed for cationic and zwitterionic (sulfobetaine) surfactant mixtures. The limits of detection for these surfactants are in the single micromolar range (1 ng N). A linear response was obtained ($R^2=0.9981$) between 50 μM and 5 mM. The methodology was then applied to the determination of an industrial zwitterionic surfactant, Rewoteric AM CAS U [coco(amidopropyl)hydroxyldimethylsulfobetaine].

Keywords: Chemiluminescent nitrogen specific detection; Detection, LC; Surfactants; Zwittergent; Rewoteric AM CAS U

1. Introduction

Surfactants are a class of compounds that are found in a multitude of domains, from industrial settings to research laboratories, to household products as well as environmental pollutants. Due to their prevalence in so many domains the need for analysis is paramount [1]. The ionic surfactants can be classified into three distinct categories depending on the charge of their hydrophilic portion. The three classifications are cationic, anionic and zwitterionic (amphoteric). This paper focuses on cationic and zwitterionic surfactants, the two classes of surfactants for which the fewest approaches for analysis exist [2–4].

Of the methods available, most are developed for and restricted to a specific class of cationic or zwitterionic surfactant. These restrictions arise either from the separation conditions or the specific post-column reaction detection schemes used. This can be illustrated by the detection scheme used for imidazoline type surfactants [5]. In the work of Kawase et al. [5] the detection was based on the identification of the reaction products of the imidazoline surfactants after they were reacted with sodium hydroxide and/or sodium chloroacetate. Other more common postcolumn reactions rely on the formation of ion-pairs which can then be detected spectroscopically [4].

In this paper, we describe a separation scheme which should be inclusive of most surfactant species. Further, this separation is combined with a detector capable of detecting all cationic and zwitterionic

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surfactants that contain nitrogen. The heart of this system is the detector, a chemiluminescent nitrogen specific detector (CLND), which allows for the specific detection of nitrogen containing species with a universal response factor dependent upon the amount of nitrogen in each analyte.

In CLND, the sample is first combusted at high temperature (>1000 °C) [6,7]:

$$\text{R–N} + \text{R–H} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NO} + \text{other combustion products} \quad (1)$$

where R–N is any chemically bound nitrogen compound and R–H is any non-nitrogenous organic compound. Subsequent reaction between ozone and nitric oxide (NO) produces nitrogen dioxide in the excited state (NO_2^*):

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* + \text{O}_2 + 47.8\ \text{kcal/mol} \quad (2)$$

(1 cal = 4.184 J). The excited nitrogen dioxide's rapid relaxation results in the release of a photon of light, between 600 and 900 nm, which is then captured and amplified in the photomultiplier tube [6–8]:

$$\text{NO}_2^* \rightarrow \text{NO}_2 + h\nu \quad (3)$$

Other combustion gases such as CO_2 and H_2O do not react with ozone to produce any discernable chemiluminescence, and so do not affect the signal. So long as the ozone in reaction (2) is in great excess, the reaction is pseudo first order for NO and so the number of photons produced are proportional to the number of NO molecules.

Thus, provided the initial combustion step (reaction (1)) is complete, this signal will be proportional to the number of nitrogen atoms originally introduced into the detector. To date, the equimolarity of the response has been demonstrated for organic compounds containing amines, amides and nitro functionalities [7] and inorganic species such as nitrate, nitrite, and cyanide [9]. Only atmospheric diatomic nitrogen does not give a chemiluminescence response [6,7]. (Azide thermally decomposes to N_2 and N, and so gives a response corresponding to only a single N [9]).

The analysis of cationic surfactants in household products using HPLC–CLND has been previously reported [10]. However, the analysis was limited to four cationic surfactants (the separation of lauryl and myrsityl monoethanolamide and the separation of lauryl and myristyl *n*-methylglucosamide). No discussion of other cationic or any zwitterionic surfactants was presented. Similarly, HPLC–CLND has also been demonstrated for ethoxyquin antioxidants [11] compounds in which the nitrogens are found in chemically similar environments to that in many surfactants.

The goal of this work was to develop an HPLC methodology that is easily adaptable to a variety of cationic and zwitterionic surfactant mixtures. Implicit within this method development is the modification of standard HPLC procedures to make them compatible with CLND. This primarily entails the elimination of any nitrogen-containing compound from the eluent, but also includes other more subtle considerations.

2. Experimental

2.1. Chemicals and materials

All solutions and eluents were prepared in Nanopure ultra-pure water (Barnstead, Duburque, IO, USA), methanol used for eluents (HPLC grade) was obtained from Fisher (Nepean, Canada). Barium chloride (99%) was from Aldrich (St. Louis, MO, USA) and triethylamine was from Fisher. The structures of the surfactants studied are shown in Fig. 1. Dodecyltrimethylammonium bromide (DTA^+, $n = 11$) (99%), tetradecyltrimethylammonium bromide

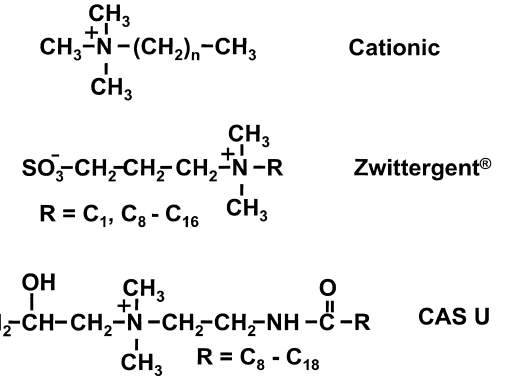

Fig. 1. Structures of surfactants studied.

(TTA^+, $n=13$) (99%) and hexadecyltrimethylammonium bromide (HTA^+, $n=15$) (99%) were all from Sigma (St. Louis, MO, USA). The zwitterionic surfactants Zwittergent 3-1 ($n=0$), Zwittergent 3-8 ($n=7$), Zwittergent 3-10 ($n=9$), Zwittergent 3-12 ($n=11$), Zwittergent 3-14 ($n=13$), Zwittergent 3-16 ($n=15$) (all reagent grade) were from Calbiochem (La Jolla, CA, USA). The industrial surfactant mixture Rewoteric AM CAS U [coco(amidopropyl)hydroxyldimethylsulfobetaine] was used as received from Witco (Dublin, OH, USA). Sodium nitrite was from BDH (Toronto, Canada). Argon (prepurified) and oxygen (ultra high purity) for the CLND were purchased from Praxair (Mississauga, Canada).

2.2. Sample preparation

All stock solutions were made to their desired concentrations in Nanopure water. Samples were prepared fresh daily in 1.5-ml centrifuge tubes and were diluted to the desired concentration with 20% methanol in water. Stock standards were kept in 15-ml Fisher-brand sterile disposable centrifuge tubes. The centrifuge tubes are made of polypropylene, thus avoiding the problems of surfactant adhesion encountered by Gerhards and Schulz [12] with the use of glass containers.

2.3. Instrumentation

Chromatographic separations with CLND were carried out on a Waters 625 LC system (Waters, Milford, MA, USA). Samples were injected using a Rheodyne 9125 injector (Rheodyne, Berkeley, CA, USA) fitted with a 20-μl polyether ether ketone (PEEK) injection loop. Connecting tubing between the injector and column was 0.005 in. I.D. PEEK (1 in. = 2.54 cm).

All separations were performed on a 100×2 mm Waters Spherisorb S3 CN column. A 30×2.1 mm Waters Sperisorb S5 CN guard column was incorporated in some experiments. The column temperature was controlled to within 0.1 °C using an Eppendorf CH-30 (Alltech, Deerfield, IL, USA) column heater equipped with a mobile phase preheater and controlled by an Eppendorf TC-50. Effluent from the column was directed to the nebulizer through a ~10 cm length of underivatized fused-silica capillary (77 μm I.D.×153 μm O.D., Polymicro Technologies, Phoenix, AZ, USA). The detector uses a zero dead volume connector (Valco, Houston, TX, USA) to join the capillary to the PEEK tubing from the column. In flow injection analysis studies, the column was removed such that the injector was connected directly to the detector.

The chemiluminescence detector was an Antek 8060 nitrogen detector (Antek Instruments, Houston, TX, USA). The furnace temperature was 1000 °C, the argon flow was 140 ml/min with an oxygen flow of 180 ml/min and the make up flow at 140 ml/min. The reaction chamber pressure was maintained at 25 Torr by the vacuum pump and the ozone flow was 30 ml/min (1 Torr = 133.322 Pa). The analyses were done with a quartz pyrolysis tube containing a ceramic insert (Antek) to handle the higher salt content of the eluent. Data was acquired at 10 Hz using a National Instrument PC-6023E data acquisition board controlled using MEASURE software (version 2.0) (National Instruments, Austin, TX, USA) on a 486 microcomputer.

Surface tension measurements were taken using a Fisher surface tensiometer Model 20 (Fisher Scientific, Pittsburgh, PA, USA). The platinum–iridium ring used was cleaned in 2-butanone and then heated in a gas flame to ensure it was free of any oil residue. The glass sample beaker was also washed with 2-butanone and rinsed with water prior to measurements.

2.4. Barium chloride cleaning

The $BaCl_2$ was found to contain nitrogen impurities, presumably in the form of $Ba(NO_2)_2$ and/or $Ba(NO_3)_2$. This was determined by FIA of $BaCl_2$, with water as an eluent, into the CLND system. The nitrogen containing anions were removed through the use of an anion-exchange column (25×4.5 cm), packed with AG 1-X4 chloride form resin (Bio-Rad, Richmond, CA, USA). Samples of the eluent from the column were monitored by flow injection analysis (FIA) with CLND to ensure the purity of the $BaCl_2$.

3. Results and discussion

3.1. Column selection

The strong hydrophobicity of surfactants results in extremely strong retention on standard reversed-phase columns, such as C_{18}. In this work, this is even more dramatic as strong organic eluents such as acetonitrile or tetrahydrofuran (THF) cannot be used. In two comprehensive reviews of the analysis of surfactants [2–4] the majority of the methods used either proprietary surfactant separation columns or cyano columns for the analysis of surfactants. It is not immediately evident however that a cyano column would be appropriate for the separation of a mixture of surfactants. Generally, cyano columns are used as a stationary phase for normal-phase separations [13]. However, cyano columns have also been successfully used in reversed-phase separations [14–17]. The retention times of hydrophobic compounds on cyano columns are similar to those on short chained reversed-phase columns (e.g. C_4 and C_8) under the same elution conditions. For instance, McCalley [18] characterized the retention of benzene on several reversed-phase columns. For a methanol–water (55:45) mobile phase, the retention factor (k) value for benzene was 1.67 on the cyano column, compared to 2.14 on a C_4 column and 3.03 on a C_8 column. The reason for this ability to retain nonpolar compounds comes from the chemistry used to bind the ligand to the silanol. In the case of cyano columns this binding is accomplished through a propyl chain [19]. When one then looks at the carbon load percentage of a cyano column we find that it is roughly half that of a C_8 column [19,20]. This clearly illustrates that the cyano column is capable of performing reversed-phase separations of hydrophobic compounds, but that the retention factors are reduced. This is exactly what is required for the separation of surfactants, since their extreme hydrophobicity leads to near irreversible retention with standard reversed-phase columns.

3.2. Nitrogen-free reversed phase HPLC

One of the key difficulties to overcome with the use of the CLND detection system is the elimination of all nitrogen from the eluent. Obviously acetonitrile cannot be used as an organic eluent. Thus other solvents must be considered. In this work, as in most others, methanol is an adequate substitute [10,21,22].

Secondary to this is the presence of any additives to the eluents. Most HPLC columns are comprised of bonded phases on a silica backbone. Silica is used due to its excellent versatility, mechanical strength, efficiency and easily controlled particle size and porosity. However, the presence of silanols on the particle surface can result in broad-tailed peaks in the analysis of basic samples. While considerable effort has been devoted to eliminating such silanol interactions, they are still very much present and of concern [18,23,24]. One approach to reducing the influence of the silanols is to add amines such as triethylamine, hexylamine and octylamine to the eluent [25–28]. However, the addition of amines to the eluent is incompatible with CLND as they would cause a high background signal.

Such silanol interactions could be avoided by using a polymeric stationary phase [29], but this would entail some loss of efficiency and mechanical strength. Further, the column is not the only source of silanols in the HPLC–CLND system. The effluent from the column must pass through a nebulizer before entering the pyrolysis chamber. The tube of the nebulizer included with the CLND is a derivatized silica capillary (~10 cm) [30]. The derivatization coating is unknown, but is suspected to be a C_{18} phase based on the retention properties of surfactants under FIA conditions. As a result, the capillary had to be replaced with a bare silica capillary of equal length. This resulted in a drastic increase in the amount of silanols present in the flow path.

Therefore, an alternate non-nitrogen containing eluent additive was needed to prevent the adsorption of the quaternary amine surfactants onto the silanols. Recently, Reta and Carr investigated the use of divalent metal cations as alternatives to amines as additives for preventing silanol interactions [25]. They found that barium chloride was comparable to triethylamine in its ability to prevent ion pairing between silanols and benzylamine. Further, barium chloride is soluble in methanol and very soluble in water [31]. Thus it may be used with methanol–water gradient based separations without fear of precipitation of the salt. Therefore, barium chloride was incorporated into the eluent for our separations

of cationic and zwitterionic surfactants. The benefit of this incorporation can be seen in the separation of a mixture of DTA^+, TTA^+ and HTA^+. In the absence of Ba^{2+} in the eluent, Fig. 2a, no peaks were observed upon injection of a mixture of cationic surfactants. Addition of 1 m*M* Ba^{2+} yielded detectable peaks. However, these were broad and irreproducible. Both 5 m*M* and 10 m*M* Ba^{2+} yielded good chromatographic behavior with the three cationic surfactants eluted within 10 min (Fig. 2b). With 5 m*M* barium a few initial injections were necessary before chromatographic behavior such as shown in Fig. 2b was observed. Some peak tailing is still evident with the 10 m*M* barium used in Fig. 2. This is consistent with Reta and Carr's observation that 10 m*M* barium gave comparable retention factors to 10 m*M* triethylamine, but with more residual peak tailing [25]. Further increases in the barium concentration were not practical. The presence of any nonpyrolytic compounds in the eluent necessitates frequent cleaning of the detector to ensure proper performance. Their presence will also shorten the life of the pyrolysis tube as well the membrane dryer which were problems that we encountered in this project as well as in previous work [9]. Using 10 m*M* barium necessitated occasional cleaning of the tube leading to the membrane drier, of the restrictor valve and of the reaction chamber, but did not otherwise compromise the CLND performance. Over longer periods of use with such salt concentrations the pyrolysis tube would need to be cleaned or replaced to remove salt deposits to ensure proper performance.

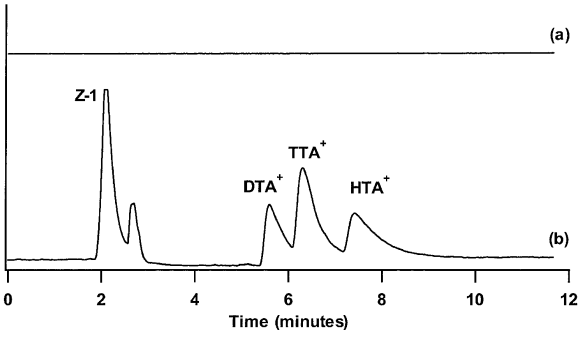

Fig. 2. Isocratic separation of cationic surfactants DTA^+, TTA^+ and HTA^+. Experimental conditions: column, Waters Spherisorb 30×2.1 mm S5 CN guard column and 100×2 mm S3 CN analytical column; eluent; (a) methanol–water (50:50, v/v), (b) containing 10 m*M* $BaCl_2$; column temperature 40.0 °C in both separations.

One unexpected discovery was that $BaCl_2$, although 99% pure, caused a significant increase in the background signal. Thus it contained significant amounts of nitrogen, presumably in the forms of $Ba(NO_2)_2$ and/or $Ba(NO_3)_2$. Purification of the $BaCl_2$ with anion-exchange as outlined in the Section 2.4 reduced the background signal six-fold.

3.3. Cationic surfactants

The mixture of cationic surfactants which was examined was comprised of DTA^+, TTA^+ and HTA^+, having the carbon chain lengths of 12, 14 and 16, respectively. We have separated these surfactants, as well as a numerous other aliphatic amines, under gradient elution conditions within 20 min (not shown). The gradient separation does allow for the identification of all the nitrogen containing species which are less hydrophobic than the surfactants as well as the surfactants themselves. Unfortunately, the gradient separation technique suffers from a low throughput capability. The separation itself is 20 min, yet the re-equilibration takes at least the same amount of time, additionally the peaks were seen to migrate based on the amount of re-equilibration which had occurred. Therefore it was concluded that an isocratic method would be best for throughput and consistency when it came to the analysis of surfactants only. Fig. 2 shows that the isocratic separation of the three cationic surfactants was accomplished within 10 min. This separation was conducted with an eluent consisting of methanol–water (50:50, v/v) as well as 10 m*M* barium chloride, the column temperature was regulated to 40.0 °C. In doing this we are now capable of at least a four-fold increase in the throughput for the analysis of surfactants relative to the gradient separation. There is no interference from less hydrophobic species in these isocratic separations, since they elute well before the surfactants of interest, as can be seen with the zwitterionic Z-1 peak.

3.4. Zwitterionic surfactants

Similar conditions were used to separate a mixture

of five zwitterionic surfactants: Zwittergent 3-8, Zwittergent 3-10, Zwittergent 3-12, Zwittergent 3-14, and Zwittergent 3-16 (Z-8, Z-10, Z-12, Z-14, Z-16), the structures of which can be seen in Fig. 1. This homologous series differs only in the length of the aliphatic chain, each one being an increase of two carbon atoms per chain over the previous form. Fig. 3 shows the separation of these five zwitterionic surfactants along with trimethylammoniumpropane-sulfonate (Z-1) which is essentially the surfactant head group. The cyano column was used with an eluent of 40% methanol in water with 10 m*M* barium chloride and a column temperature of 40.0 °C. All components are near baseline resolved within 10 min.

To the best of our knowledge, Fig. 3 is the first published HPLC separation of a homologous series of zwitterionic surfactants. The detector response factor (i.e. peak area divided by molar concentration) varied only 15% over the six components in Fig. 3. This is slightly higher than the 6% relative standard deviation we saw with this detector for inorganic species [9]. The greater variation may be the result of peak tailing leading to challenges in peak area assesment. An excellent choice as an internal standards for the quantification of the surfactants for this separation are nitrate and nitrite which elute before the Z-1 peak.

3.5. Linear range and limit of detection

One of the advantages of CLND is its wide linear range, quoted to be five orders of magnitude [6,7].

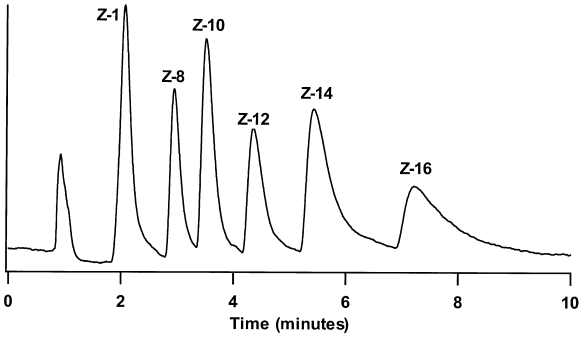

Fig. 3. Isocratic separation of zwitterions Z-1, Z-8, Z-10, Z-12, Z-14 and Z-16. Experimental conditions as in Fig. 2 except the eluent is methanol–water (40:60, v/v) with 10 m*M* $BaCl_2$.

This offers a great advantage for industrial monitoring of any nitrogen-containing product, since this reduces the need for dilutions. However, if the critical micelle concentration (CMC) is exceeded then surfactants are present both as free surfactants and in micelles. While micelle formation would not be expected to alter the CLND response, it may cause additional band broadening which could affect the linearity of calibrations performed using peak height. Therefore the using the isocratic method described in Section 3.4, the linearity of the response was tested using Z-12. The CMC for Z-12 is 2–4 m*M* in 50 m*M* Na^+ (the counter ion is unspecified) in water [32]. Similarly, a plot of surface tension vs. surfactant concentration (not shown) indicated that the CMC of Z-12 in 20% methanol was 3.6 m*M*. Thus the peak height was monitored for Z-12 concentrations ranging from 50 μ*M* to 5 m*M*, where the surfactant is present in the micelle form at the upper portion of the calibration range.

A plot of peak height vs. concentration was linear ($R^2 = 0.9981$) over the entire range studied (50 μ*M*–5 m*M*) with an intercept equal to zero at the 95% confidence interval. That the response at the highest concentrations remained linear shows that an accurate analysis of the surfactant can be accomplished even when its concentration exceeds the CMC.

Under the conditions discussed in Sections 3.4 and shown in Fig. 3, the limit of detection for Z-12 is 8 μ*M*. This is comparable with the previously reported detection limit of 1 ng-N (approximately 3 μ*M* for compounds containing a single nitrogen), observed for a variety of compounds [9]. As the limit of detection for CLND is based on the amount of nitrogen in the analyte molecule, the detection limit for other zwitterionic and cationic surfactants would be in the single-digit micromolar range. The detection limits will improve with shorter hydrophobic chain lengths, due to improved peak shapes.

3.6. Gradient separation of zwitterionic surfactants

One of our goals in developing this method was to be able to determine the composition of an industrial surfactant mixture known as Rewortic CAS U (Fig. 1c). This surfactant mixture has been used by our research group to control the electroosmotic flow (EOF) in capillary electrophoresis [33–35].

It was known that the surfactant was synthesized using coconut oil as a starting material. The nature of the surfactant source will affect the chain lengths available as well as the distribution of the different lengths. Products from palm oil are mostly C_{16} and C_{18} with trace amounts of C_{14}, coconut oils however produce chain lengths from C_6 to C_{18} (in two-carbon increments) [36]. Therefore in knowing that the surfactant mixture can contain these possible chain lengths the analysis was facilitated.

The only previous analytical method reported for monitoring of a similar coconut derived surfactant, cocamidopropylbetaine (CAPB), used HPLC–electrospray ionisation (ESI) MS [28]. For their analysis the surfactants were separated, with the C_{14} form eluting after 30 min, by reversed-phase HPLC. The ESI analysis was performed in both the positive and negative ion modes. The MS analysis revealed the formation of dimer and trimer clusters from the ESI source in both modes, which can be problematic for analysis. The formation of doubly charged species and cleaved stable fragments were also problematic. The analysis can be accomplished but is prone to challenges from inorganic salts in the positive ion mode, which can be overcome with the less sensitive negative ion mode.

Given the wide range of hydrophobicity in this surfactant mixture, gradient elution was used. The gradient was linear from 25 to 65% methanol over a 10-min period, with a constant 10 m*M* barium chloride. With this HPLC system the dwell time of the eluent before it reaches the column, at this flow-rate, is approximately 9 min. Thus the first 9 min of this separation were performed under isocratic conditions, equivalent to the initial gradient conditions. Fig. 4 shows the resultant chromatogram. This clearly shows a good separation ($R_s \geq 1.9$) of all the nitrogen containing components of the surfactant, with no evidence of overlapping peaks. Thus a clear identification of the components can be made.

In Fig. 4, the C_{12} is the most abundant homolog followed by the $C_{14.}$ Further, assuming equimolar response their relative abundances are 49.0 and 19.5%, respectively. These are in good agreement with the 48.0 and 19.0% expected from a coconut oil base [36]. Again, assuming equimolar response, the average molecular mass for the mixture was determined to be 428 g/mol. This is comparable to the 450 g/mol obtained through a gas chromatographic analysis [34]. The agreement between these two methods illustrates how well this system works for the analysis of the composition of an unknown surfactant mixture.

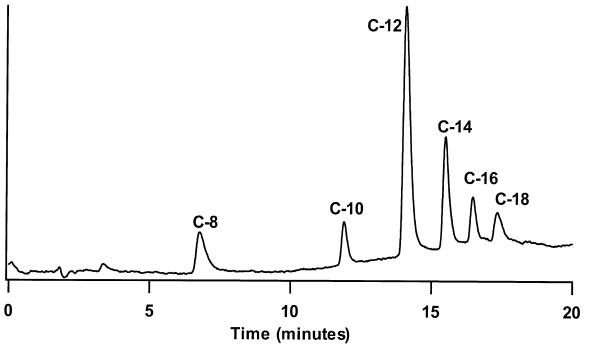

Fig. 4. Gradient separation of the industrial zwitterionic surfactant mixture Rewoteric AM CAS U. Experimental conditions as in Fig. 2, except no guard column was present and eluent, linear gradient of 25–65% (v/v) methanol in water over 10 min, constant 10 m*M* $BaCl_2$; column temperature, ambient; analyte concentration ~200 μ*M* (above CMC).

4. Conclusions

The universal CLND response allows for the analysis and quantification of both cationic and zwitterionic surfactants without the need for any postcolumn reagents or significantly different chromatographic conditions. We have illustrated two highly effective separation techniques for the separation of both surfactant forms, allowing for high versatility, without the need for any modification of the detection system. Finally the limit of detection of these surfactants is in the low micromolar range, with a linear range ($R^2 = 0.9981$) which remains linear even when the concentration of the surfactant exceeds the CMC. Thus, HPLC–CLND is a powerful methodology for determination of cationic and zwitterionic surfactants.

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