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Determination of homologues of quaternary ammonium surfactants by capillary electrophoresis using indirect UV detection

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Abstract

This investigation describes the simultaneous separation of two major non-chromophoric quaternary ammonium surfactants, alkyltrimethyl- and dialkyldimethylammonium compounds (ATMACs and DADMACs, respectively), by capillary electrophoresis (CE) using indirect UV detection. The most effective separation conditions was 10 mM phosphate buffer with 57.5% tetrahydrofuran and 3 mM sodium dodecyl sulfate (SDS) at pH 4.3, and the sample hydrodynamic injection of up to 20 s at 1 psi (approximately 60 nl), and an applied voltage of 25 kV (1 psi = 6.9 kPa). Specially, the selection of an appropriate chromophore and an internal standard (I.S.) to improve the peak identification and quantitation was systematically investigated. Decylbenzyldimethyl ammonium chloride (C_{10}-BDMA$^+$C$^-$) as a chromophore with 3 mM sodium dodecyl sulfate provided the best detectability for all homologues. The reproducibility of the migration time and quantitative analysis can be improved by using tetraoctyl ammonium ion as an internal standard, giving the relative standard deviation (R.S.D.) less than 0.8% for the relative migration times, and 2.5–5.5% for the relative peak areas. A good linearity of CE analysis was obtained in the range of 1.0–20 μg/ml with r^2 values of above 0.999. The analysis of cationic surfactants in commercial products of hair conditioners and fabric softeners was also performed. Electrospray mass spectrometric method was applied to evaluate the CE method, and the compatible results were obtained.

Keywords: Surfactants; Quaternary ammonium compounds

1. Introduction

Alkyltrimethyl- and dialkyldimethylammonium compounds (ATMACs and DADMACs, respectively) are two major non-chromophoric quaternary ammonium surfactants, and are widely used in industrial applications and pharmaceutical/cosmetic preparations. Moreover, these cationic surfactants are also the main ingredient of hair conditioners and fabric softeners, which imparts softness, manageability, and antistatic properties to hair and fabrics. They typically contain various proportions of linear alkyl homologues of C_{12}, C_{14}, C_{16}, and C_{18} with a polar head group and non-chromophoric substituent. Each of them possess different physical, chemical, and microbiological properties. The proportion of these homologous in the mixture determines its effectiveness as a softness and disinfectant. In order to monitor product control, formulation and application, it is necessary to develop convenient and appropriate analytical techniques for the separation and detection of these quaternary ammonium surfactants.

It is difficult to determine these non-aromatic cationic surfactants because of their lack of chromophores, their polarity, and ease of forming micelles by long alkyl chain at low concentration and thermal instability. The determination of these compounds has been performed commonly by diverse techniques, such as two-phase titration [1,2], spectrophotometry [3–5], gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS) by converting quaternary ammonium salts into the corresponding tertiary amines [6–12]. Fast atom bombardment mass spectrometry (FAB-MS) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) techniques have been applied to analyze relatively high concentrations of these surfactants in pharmaceutical formulations, ophthalmic products, and healthcare products [13–18]. High-performance liquid chromatography (HPLC) is the most promising method for analyzing alkyl benzyl cationic surfactants, but the analysis of these non-chromophoric surfactants is problematic, requiring

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electrical conductivity detection [19–21], post-column detection [22,23] or indirect photometric detection [24]. However, the distinction between different homologues of ATMACs and DADMACs is difficult because the complete chromatographic separation of all homologues is nearly impossible. Currently, capillary electrophoresis (CE) has become one of the most powerful separation techniques in analyzing large numbers of ionic species (see [25,26] and the references cited therein). It is preferred in many applications to conventional chromatographic techniques because CE leads to high separation power, requires small sample volumes, consumes minimal organic solvent, and provides rapid method development (see [27,28] and the references cited therein). The CE has been shown to offer higher resolution separation than does HPLC for ionic surfactants, the duration of the analysis is short, easy for indirect photometric detection, minimum solvent consumption, and inexpensive column replacement [29–35].

The purpose of this study was to develop and validate a modified CE method using indirect UV detection to routinely determine the homologue of ATMAC and DADMAC simultaneously in commercial products of hair conditioners and fabric softeners. This study examined the influences of CE separation conditions, such as organic solvent in sample solution, organic modifier content, buffer concentration, and buffer pH. Specifically, the selection of an appropriate chromophore and an internal standard (I.S.) to enhance peak identification and quantitation also was systematically examined. Additionally, the results were confirmed using the electrospray mass spectrometric method (ESI-MS) to identify the occurrence of $ATMA^+$ and $DADMA^+$ homologues in the real samples.

2. Experimental

2.1. Chemicals and reagents

Unless stated otherwise, all high purity chemicals and solvents were purchased from Aldrich (Milwaukee, WI, USA), Tedia (Fairfield, OH, USA), and Merck (Darmstadt, Germany), and were used without further purification. Selected eight cationic surfactant analytes, four chromophores and four internal standards in this study are listed in Table 1. Sodium dodecyl sulfate (SDS) was from Merck. Sodium dihydrogen phosphate monohydrate (NaH_2PO_4) separation buffer was prepared at stated concentrations between 5 and 20 mM in deionized water and were adjusted to stated pH between 3 and 6. Stock solutions of these analytes (1000 μg/ml) were prepared in methanol. Working standard solutions were obtained by diluting the stock standard solution with various percentage of methanolic solution (between 60 and 100%, 90% being optimal, see Section 3) to appropriate concentrations. Deionized water was further purified with a Millipore water purification device (Millipore, Bedford, MA, USA).

Table 1
Selected cationic surfactant analytes, chromophores, and internal standards in this study

Name (abbreviation) of chemical
Cationic surfactant analytes
Dodecyltrimethyl ammonium bromide (C_{12}-TMA^+B^-, 99% purity)[a]
Myristyltrimethyl ammonium bromide (C_{14}-TMA^+B^-, >97% purity)[b]
Hexadecyltrimethyl ammonium bromide (C_{16}-TMA^+B^-, 98% purity)[c]
Octadecyltrimethyl ammonium bromide (C_{18}-TMA^+B^-, >97% purity)[b]
Didodecyldimethyl ammonium bromide (di-C_{12}-DMA^+B^-, >97% purity)[b]
Ditetradecyldimethyl ammonium bromide (di-C_{14}-DMA^+B^-, >97% purity)[b]
Dihexadecyldimethyl ammonium bromide (di-C_{16}-DMA^+B^-, >97% purity)[b]
Dioctadecyldimethyl ammonium bromide (di-C_{18}-DMA^+B^-, >97% purity)[b]
Chromophores
Decylbenzyldimethyl ammonium chloride (C_{10}-BDMAC, >98% purity)[c]
Dodecylbenzyldimethyl ammonium chloride (C_{12}-BDMAC, >98% purity)[d]
Tetradecylbenzyldimethyl ammonium chloride (C_{14}-BDMAC, >98% purity)[b]
Hexadecylbenzyldimethyl ammonium chloride (C_{16}-BDMAC, >98% purity)[b]
Internal standards
Methyltrioctyl ammonium bromide ($MTOA^+B^-$, >98% purity)[b]
Tetraheptyl ammonium bromide (THA^+B^-, >98% purity)[b]
Tetraoctyl ammonium bromide (TOA^+B^-, >98% purity)[c]
Tetrakis(decyl) ammonium bromide ($TKDA^+B^-$, >98% purity)[c]

[a] From Sigma (St. Louis, MO, USA).
[b] From Aldrich (Milwaukee, WI, USA).
[c] From Fluka (Buchs, Switzerland).
[d] From ChemServices (West Chester, PA, USA).

2.2. Instrumentation and separation conditions

2.2.1. Capillary electrophoresis

All experiments were performed on a P/ACE MDQ system (Beckman–Coulter, Fullerton, CA, USA) equipped with a UV-Vis detector. Separations were carried out in an untreated fused-silica capillary (J&W Scientific, Folsom, CA, USA) of 50 μm i.d. and an effective length of 30 cm (total length 40 cm). Before use, the new capillary was conditioned with methanol for 10 min at 25 °C, followed by 10 min with deionized water, and 20 min 1 M NaOH, then rinsed capillary with deionized water for 10 min, and followed by 20 min 1 M HCl, 10 min with deionized water, and 20 min separation buffer. Between runs, the capillary was flushed with deionized water 2 min at 25 °C, followed by 2 min methanol, 1 min deionized water, then 1 M NaOH for 2 min, and deionized water for 1 min, and followed by 1 M HCl for 2 min, and deionized water for 1 min before run. This procedure improved peak sharps and the reproducibility of migration time. All samples were hydrodynamically injected into the capillary in 20 s at 1 psi (1 psi = 6.9 kPa), a volume of approximately 60 nl, and an applied voltage of

25 kV. The UV detector was operated at 214 nm. All electrophoresis runs were performed at temperature 25 °C. The on-column detection window was made by burning a small section (ca. 3 mm) of the external polymide coating and scraping off the burned residue with methanol. The pH of solutions was measured by a Mettler-Toledo MP220 pH meter (Schwerzenbach, Switzerland).

2.2.2. Electrospray mass spectrometry

Electrospray mass spectrometry was used to confirm the results and identify the homologues of quaternary ammonium surfactants in commercial products. The positive ion electrospray mass spectra were acquired on an Agilent LC/MSD SL ion trap mass spectrometry (Agilent Technologies, Palo Alto, CA, USA), equipped with electrospray ionization probe. The operating conditions of MS system were optimized in full-scan mode (*m/z* scan range 100–700) by flow injection analysis of each analyte at 0.1 μg/ml concentration. The maximum ion accumulation time was 300 ms. Samples were dissolved in methanol (containing 5 mM ammonium formate) at appropriate concentrations and directly infused to ESI-MS.

2.3. Sample preparation

The hair conditioners and liquid fabric softeners were purchased from local supermarkets, and then were diluted with methanolic solution (90%, v/v) directly to appropriate concentrations. To prevent capillary blockage, all solutions and samples were filtered through 0.45 μm membrane filter (Gelman Scientific, Ann Arbor, MI, USA) prior to use.

3. Results and discussion

3.1. Evaluation of separation conditions

3.1.1. Organic solvent in a sample solution and a separation buffer

The formation of micelles and adsorption onto the capillary surface are critical factors for the influence the separation of quaternary ammonium surfactants with the long alkyl group [29,34]. According to a previous report, an appropriate concentration of methanol must be added to disrupt the micelles in the sample solution to achieve effective separation of alkylbenzyldimethyl ammonium compounds (ABDMACs) with the long alkyl group [29]. Fig. 1 shows the effect of methanol concentration in the sample solution for the effectiveness of the separation of $ATMA^+$ and $DADMA^+$ homologues with a 10 mM phosphate buffer containing 50% tetrahydrofuran (THF) and 3 mM C_{10}-BDMAC as a chromophore at pH 4.3. The addition of 50% methanol in the sample solution completely disrupts micelles of all four $ATMA^+$ homologues and di-C_{12}-DMA^+, partially disrupts micelles of di-C_{14}-DMA^+, and causes no disruption for micelles of di-C_{16}-DMA^+ and di-C_{18}-DMA^+. The degree of

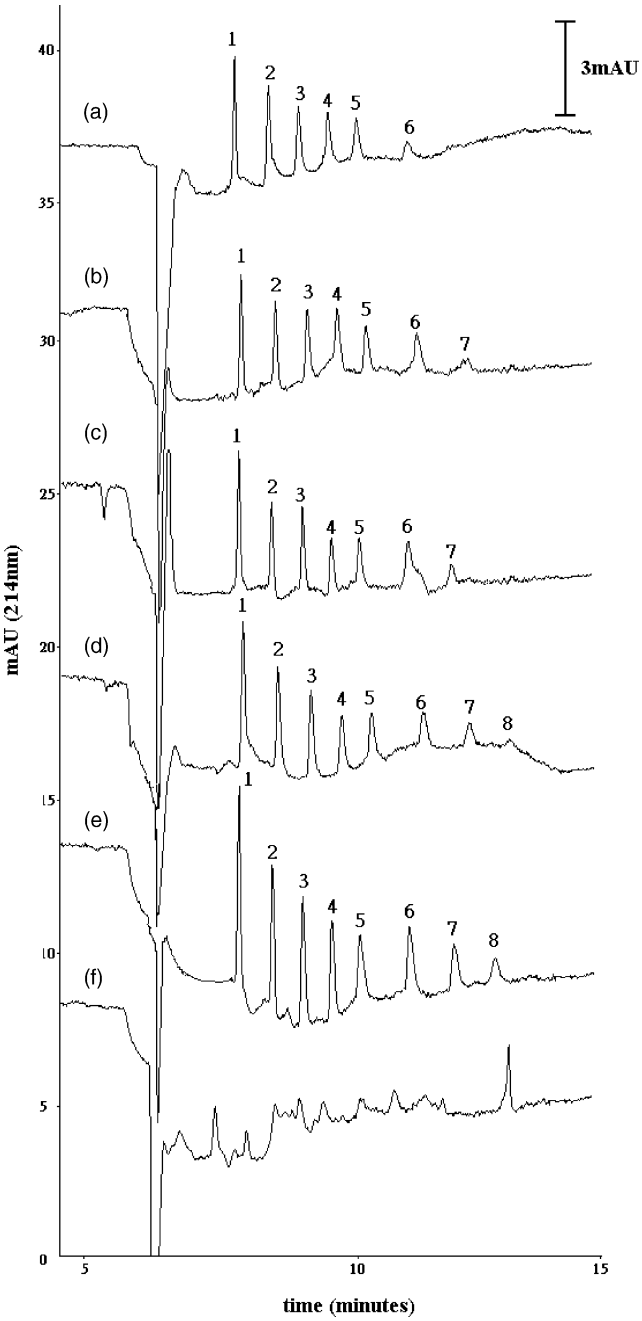

Fig. 1. Effect of methanol added in varied proportions (v/v) to a sample solution: (a) 50%, (b) 60%, (c) 70%, (d) 80%, (e) 90%, and (f) 100%. Standard mixture containing 5.0 μg/ml each of (1) C_{12}-, (2) C_{14}-, (3) C_{16}-, (4) C_{18}- TMA^+ homologues, and (5) di-C_{12}-, (6) di-C_{14}-, (7) di-C_{16}-, (8) di-C_{18}- DMA^+ homologues; separation buffer 10 mM NaH_2PO_4 (pH 4.35), 3 mM SDS, 50% THF and 3 mM C_{10}-BDMAC (as a chromophore); voltage, 25 kV; temperature, 25 °C; detection wavelength, 214 nm; hydrodynamic injection at 1 psi for 20 s.

disruption of micelles of $DADMA^+$ homologues increased significantly as the proportion of methanol in the sample solution increased from 60 to 80%. When methanol in the sample solution reached 90%, better resolution and improved peak shapes were obtained within 13 min for all the homologues of $ATMA^+$ and $DADMA^+$ (Fig. 1e). However,

in pure methanol (Fig. 1f), all the peaks are distorted due to micelles reformation in polar non-aqueous solvents. The similar phenomenon was observed for ABDMACs dissolved in pure methanol or acetonitrile owing to increased solvophobic interaction of the hydrocarbon tails of surfactants [29]; thus micelles appear more effectively be disrupted in aqueous methanol (90%, v/v) than in pure methanol.

Moreover, adding organic solvents to modify the separation buffer is also essential for both solubility and obtaining efficient separation between the homologues of quaternary ammonium surfactants [34,35]. A high concentration of organic solvent in the buffer was recommended to ensure sufficient peak resolution of the $ATMA^+$ and $DADMA^+$ homologues. We found a 50% THF composition in the buffer given a reasonable separation between the analysis time and resolution of the cationic homologues.

3.1.2. Chromophores

Owing to the lack of any chromophoric groups on these cationic surfactants, appropriate chromophoric cation selection in the separation buffer must be evaluated for indirect UV detection. The chromophore should have a high molar absorptivity and a similar mobility like the analytes in order to enhance the sensitivity. The difference in

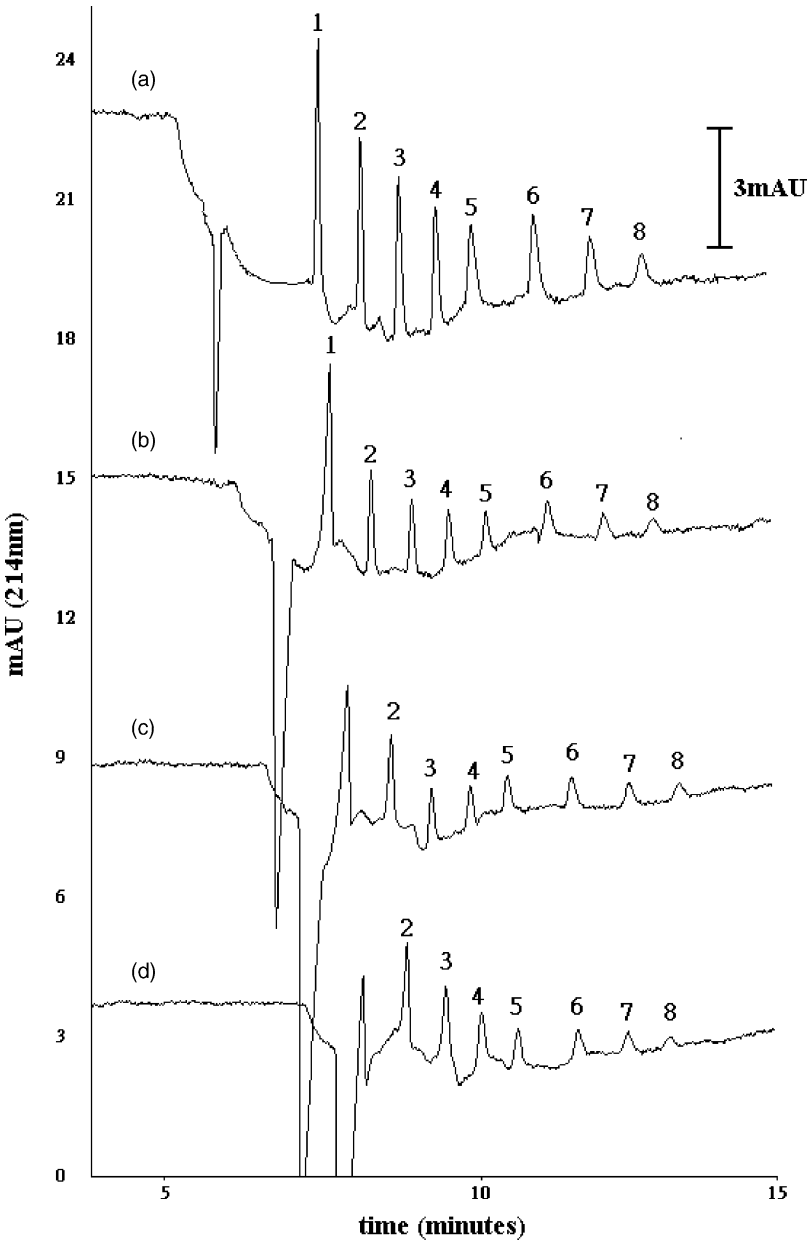

Fig. 2. Comparison of separation and peak shape of $ATMA^+$ and $DADMA^+$ homologues using alkylbenzyldimethyl ammonium chlorides (3 mM) as chromophores: (a) C_{10}-, (b) C_{12}-, (c) C_{14}-, and (d) C_{16}-benzyldimethyl ammonium chlorides. Peak numbering and experimental conditions as given in Fig. 1.

electrophoretic mobilities of the analytes and chromophores may create a peak tailing [36]. Various organic cations with chromophoric groups have been tested, and dodecylbenzyldimethyl ammonium chloride (C_{12}-BDMAC) provided the best detection sensitivity and peak shape for ATMACs, as reported elsewhere [35]. Fig. 2 shows a comparison of the separation of $ATMA^+$ and $DADMA^+$ homologues using C_{10}- to C_{16}-benzyldimethyl ammonium chlorides (C_{10}- to C_{16}-BDMAC) as chromophores in separation buffers. Separation of solvent peak and C_{12}-TMA^+ was optimized with C_{10}- or C_{12}-BDMAC as chromophore. When C_{14}- and C_{16}-BDMAC were used, the solvent peaks obscured the peak C_{12}-TMA^+, and distorted the peak shapes of all homologues (Fig. 2c and d). The results indicated that better detection sensitivity and separation were achieved when C_{10}-BDMAC was used as the chromophore (Fig. 2a), which

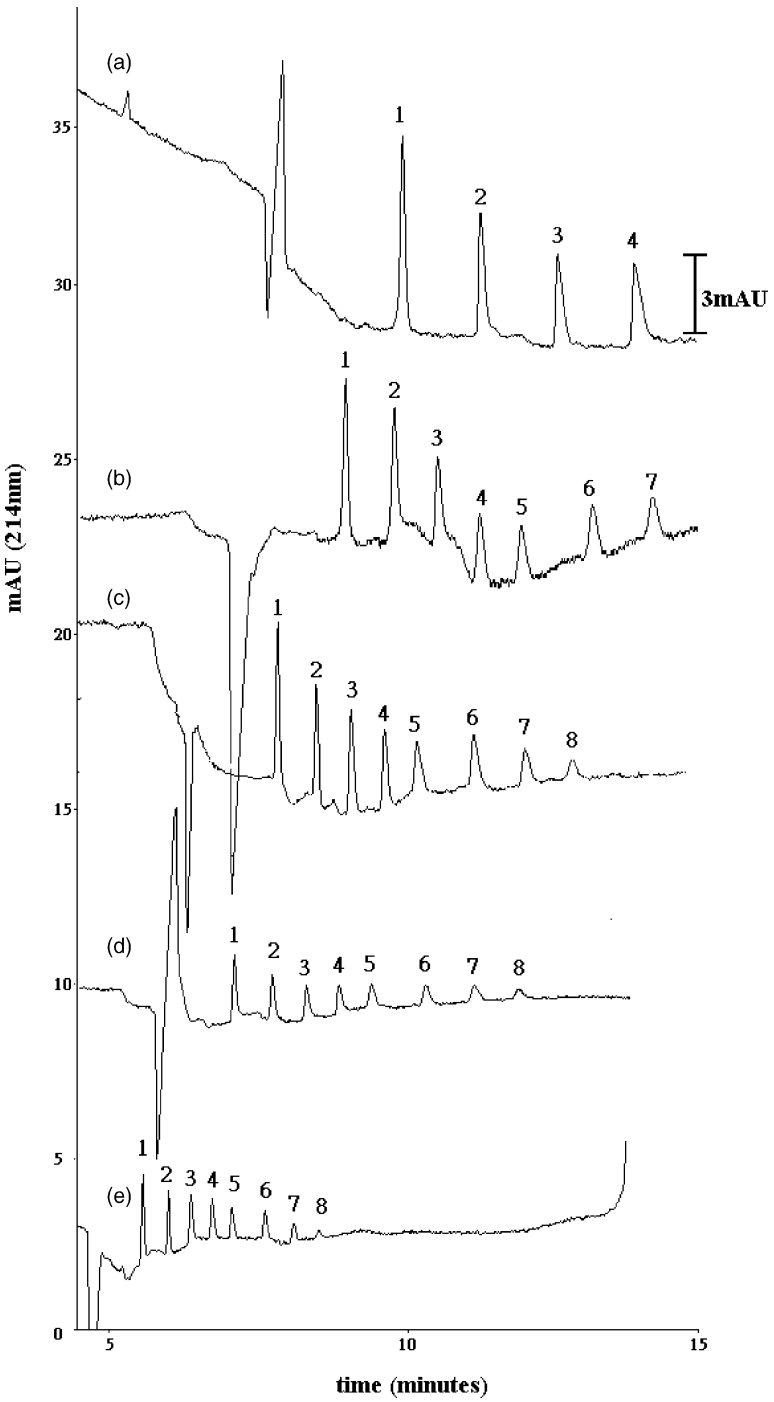

Fig. 3. Effect of pH on the separation of $ATMA^+$ and $DADMA^+$ homologues: (a) pH 3, (b) pH 4, (c) pH 4.3, (d) pH 5, and (e) pH 6. Peak numbering and experimental conditions as given in Fig. 1.

is suitable for obtaining accurate quantitation and calibrations. Fig. 2 also illustrates that the peak response depended on the mobility match between the analyte and the chromophore. When the chromophore and the analyte have the same mobility, a one-to-one displacement can enhance sensitivity [37]. The peak heights and shapes of the first four peaks (all $ATMA^+$ homologues) are better than those of the $DADMA^+$ homologues, possibly due to a close mobility match for C_{10}-BDMAC. The addition of SDS was necessary to improve the peak resolution due to the formation of ion pairs with the cationic analytes [35]. However, SDS may lead to peak broadening and signal intensity decreasing. In this study, chromophore C_{10}-BDMAC with 3 mM SDS in separating buffer enabled all of the homologues to be separated in a reasonable migration times and signal intensity.

3.1.3. Buffer pH and concentrations

Buffer pH plays an important role in CE separation because it influences both analyte charge and electro osmotic flow (EOF) strength. The mobility of cationic surfactants increased significantly with increase in pH from 3 to 6 (Fig. 3). However, the peak response decreased with increasing pH, a phenomenon can be explained in terms of the capillary surface being highly charged in the higher pH buffer, and more cationic surfactants being absorbed tightly to the negatively charged silica owing to coulombic interactions. Therefore, reducing buffer pH was suggested as a means of decreasing or minimizing the adsorption of cationic surfactants onto the surface. The results reveal a clear trade off between analysis time and peak response, which can be achieved by using buffer pH of around 4.3. The influence of the buffer

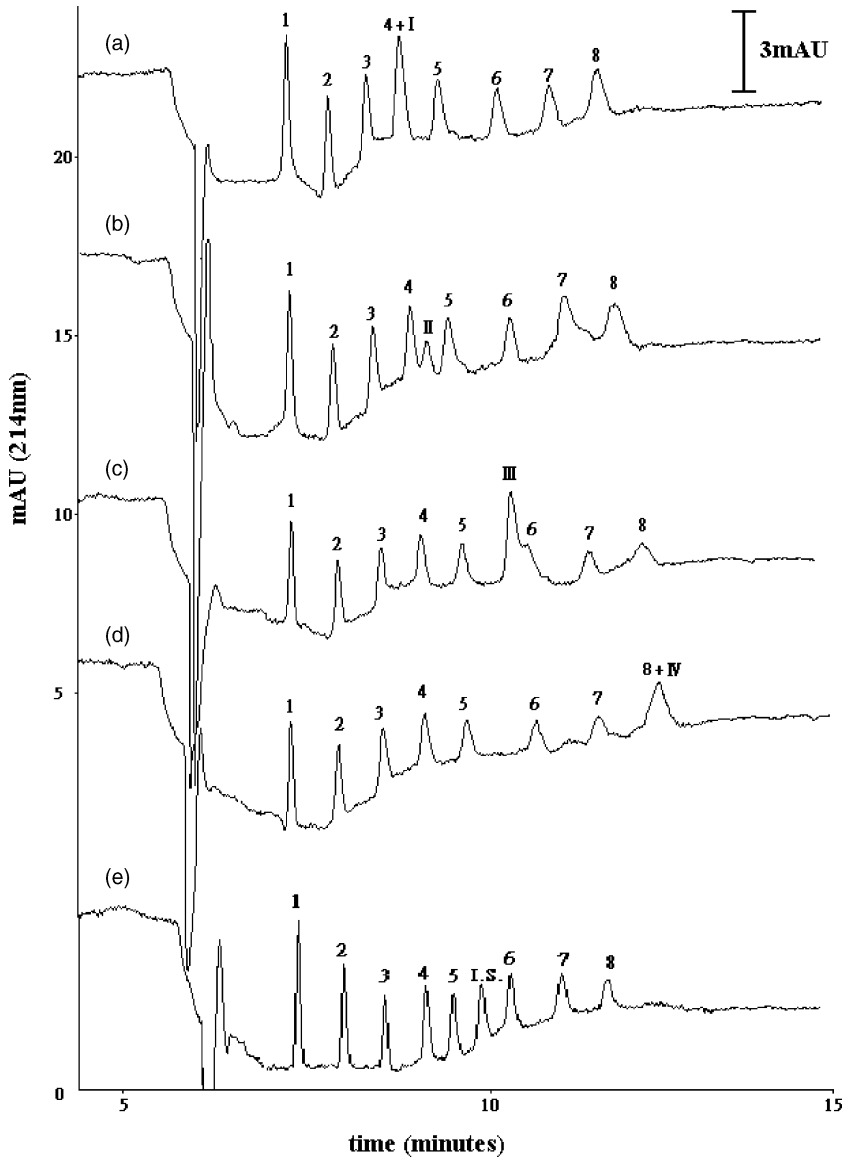

Fig. 4. Comparison of the separation of four internal standards (I.S.) among the $ATMA^+$ and $DADMA^+$ homologues in electropherograms: (a) I.S.-I, $MTOA^+$, (b) I.S.-II, THA^+, (c) I.S.-III, TOA^+, (d) I.S.-IV, $TKDA^+$, and (e) same as (c) except THF content increased to 57.5%. Peak numbering and experimental conditions as given in Fig. 1.

concentration on the migration time and separation of cationic surfactants was also examined in the range between 5 and 20 mM of phosphate buffer at pH 4.3 with 50% THF. The migration time and resolution for these cationic homologues did not differ significantly in the range between 10 and 20 mM (results not shown).

3.1.4. Internal standards

Internal standards can be used to improve the reproducibility of the migration time and quantitative analysis, as reported previously [38–41]. The I.S. peak should be clearly separated from the peaks of all other components of the sample, and the resolution ideally should exceed 1.25 [42]. The best position of the I.S. peak also should not be too far from the analyte peaks, and is best located in the middle of all the analyte peaks. Figs. 1–3 shows that sufficient space exists to locate the I.S. peak between peaks 5 and 6. Fig. 4 compares the separation of four internal standards among the middle of the analytes in the electropherograms. Only the internal standard-III (TOA^+) migrates between peaks 5 and 6, but with poor resolution (Fig. 4c). However, increasing THF from 50 to 57.5% can improved the resolution, and the resolution with peak 6 can reached to 2.6, as illustrated in Fig. 4e. In this study, the most effective separation was achieved by 10 mM phosphate buffer with 57.5% tetrahydrofuran and 3 mM SDS at pH 4.3, and the sample hydrodynamic injection of up to 20 s at 1 psi (approximately 60 nl), and an applied voltage of 25 kV and 25 °C.

3.2. Method validation and applications

To validate the performance of the CE separation, the reproducibility (in terms of relative standard deviation, R.S.D.) and linearity with standard solution mixtures under the optimum conditions described above was studied. Table 2 summarizes the R.S.D. in migration times, peak areas, relative migration times and relative peak areas, as well as linearity of response. The reproducibility of the technique was tested using eight replicate injections of $ATMA^+$ and $DADMA^+$ standard mixture (5.0 μg/ml each). The R.S.D. of the migration times and peak areas were around 1.1–2.2% and 3.7–6.2%, respectively, however, they were improved significantly when internal standard was used, especially for the R.S.D. of migration times (0.1–0.8%). Calibration for $ATMA^+$ and $DADMA^+$ homologues was performed in the concentration range between 1.0 and 20 μg/ml (in five-level). Using TOA^+ as an internal standard, the response factors were calculated by the peak areas of $ATMA^+$ and $DADMA^+$ homologues relative to fixed concentration of TOA^+. The precision of the curve, as indicated by the R.S.D. of response factors ranged from 2.3 to 6.5%. The calibration curves were linear with coefficients of determination $r^2 > 0.999$. The R.S.D. of the relative migration time was around 0.2–0.6% when various concentrations of $ATMA^+$ and $DADMA^+$ homologues were injected. The numbers of theoretical plates per meter measured in this work are typically in the range 111,000 (for di-C_{18}-DMA^+B^-)–177,000 (for C_{12}-TMA^+B^-). These results demonstrate that the CE analysis for $ATMA^+$ and $DADMA^+$ homologues provides high reproducibility and excellent linearity. The quantitation limits for $ATMA^+$ and $DADMA^+$ homologous are found to be 0.05–0.1 and 0.1–0.5 μg/ml, respectively.

Five hair conditioners and five liquid fabric softeners were employed as test samples after appropriate dilutions. Table 3 lists the contents of $ATMA^+$ and $DADMA^+$ homologues found in these commercial products. Fig. 5 shows the typical electropherograms of CE obtained for $ATMA^+$ and $DADMA^+$ homologues standards and real samples of hair conditioner-E and liquid fabric softener-D. The presence of the C_{16}- and C_{18}-TMA^+ homologues and di-C_{16}- and di-C_{18}-DMA^+ homologues were measured for all liquid fabric softeners, probably due to their greater softening and antistatic properties, and the total content ranging from 1.78 to 3.07%. For hair conditioners, the variation in the homologous distribution from different manufacturers was observed with the total $ATMA^+$ content (no $DADMA^+$

Table 2
Reproducibility, linearity of response, and response factors

	Compound							
	C_{12}	C_{14}	C_{16}	C_{18}	Di-C_{12}	Di-C_{14}	Di-C_{16}	Di-C_{18}
Reproducibility ($n = 8$, 5.0 μg/ml of each)								
Migration time (R.S.D., %)	1.1	1.3	1.4	1.6	1.7	1.8	2.0	2.2
Peak area (R.S.D., %)	3.7	4.4	3.9	4.5	4.2	6.2	4.8	5.5
Relative migration time (TOAB as I.S.) (R.S.D., %)	0.8	0.5	0.4	0.3	0.1	0.1	0.3	0.5
Relative Peak area (R.S.D., %)	3.0	2.5	3.6	2.5	4.5	5.5	4.8	4.6
Linearity of response[a]								
Correlation coefficient (r^2)	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
Response factor (TOAB as I.S.) (R.S.D., %)	2.3	5.6	5.4	5.0	6.5	2.5	5.3[b]	2.9[c]
Relative migration time (R.S.D., %)	0.6	0.2	0.2	0.3	0.6	0.5	0.6	0.6
Quantitation limit (μg/ml)	0.05	0.05	0.1	0.1	0.1	0.1	0.2	0.5

[a] Concentration range from 1 to 20 μg/ml (five-level).
[b] Concentration range from 2 to 20 μg/ml for di-C_{16}DMAC (four-level).
[c] Concentration range from 5 to 20 μg/ml for di-C_{18}DMAC (three-level).

Table 3
The contents of $ATMA^+$ and $DADMA^+$ homologues found in hair conditioners and fabric softeners

Sample	$ATMA^+$ (%)				$DADMA^+$ (%)			
	C_{12}	C_{14}	C_{16}	C_{18}	Di-C_{12}	Di-C_{14}	Di-C_{16}	Di-C_{18}
Hair conditioner-A	0.02	0.03.	1.90	0.2	n.d.	n.d.	n.d.	n.d.
Hair conditioner-B	0.13	n.d.	0.89	n.d.	n.d.	n.d.	n.d.	n.d.
Hair conditioner-C	n.d.	0.05	0.04	0.08	n.d.	n.d.	n.d.	n.d.
Hair conditioner-D	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	n.d.	n.d.
Hair conditioner-E	n.d.	n.d.	0.73	n.d.	n.d.	n.d.	n.d.	n.d.
Fabric softener-A	n.d.	n.d.	0.02	0.08	n.d.	n.d.	0.61.	1.29
Fabric softener-B	n.d.	n.d.	0.05	0.09	n.d.	n.d.	0.48.	1.24
Fabric softener-C	n.d.	n.d.	0.03	0.11	n.d.	n.d.	0.41	1.23
Fabric softener-D	n.d.	n.d.	0.09	0.19	n.d.	n.d.	1.09	1.48
Fabric softener-E	n.d.	n.d.	0.16	0.23	n.d.	n.d.	1.10	1.58.

n.d. not detected at method quantitation limits.

homologues were detected) ranging from 0.14 to 2.15% (although the homologous distributions were not given by the manufacturers). The peak identification and quantitation were performed by relative migration times and response factors, respectively, using TOA^+ as an internal standard.

ESI-MS analysis was used to confirm the occurrence of $ATMA^+$ and $DADMA^+$ homologues in hair conditioners and liquid fabric softeners. Since solutions already contain the cationic surfactants in ion forms, the mass spectra only comprise the signals of the molecular cations. Therefore, the ESI mass spectrum of standard mixture shows their intense molecular ions of *m*/*z* 228.3, 256.3, 284.4, and 312.5, corresponding to the $ATMA^+$ homologues; and *m*/*z* 382.5, 438.6, 494.6, and 550.7, corresponding to the $DADMA^+$ homologues, respectively (Fig. 6a). The small ion at *m*/*z* 522.6 and the intense ion at *m*/*z* 578.7 correspond to the mono-C_{16}/C_{18}-DMA^+ and mono-C_{18}/C_{20}-DMA^+, respectively. The homologue patterns in CE electropherograms (Fig. 5) agreed well with the pattern of ESI mass spectra (Fig. 6). Notably, no multiply charged ions and adduct formation with background ions such as Na^+, K^+, etc. are present [43]. Moreover, CE analysis also reveals the presence

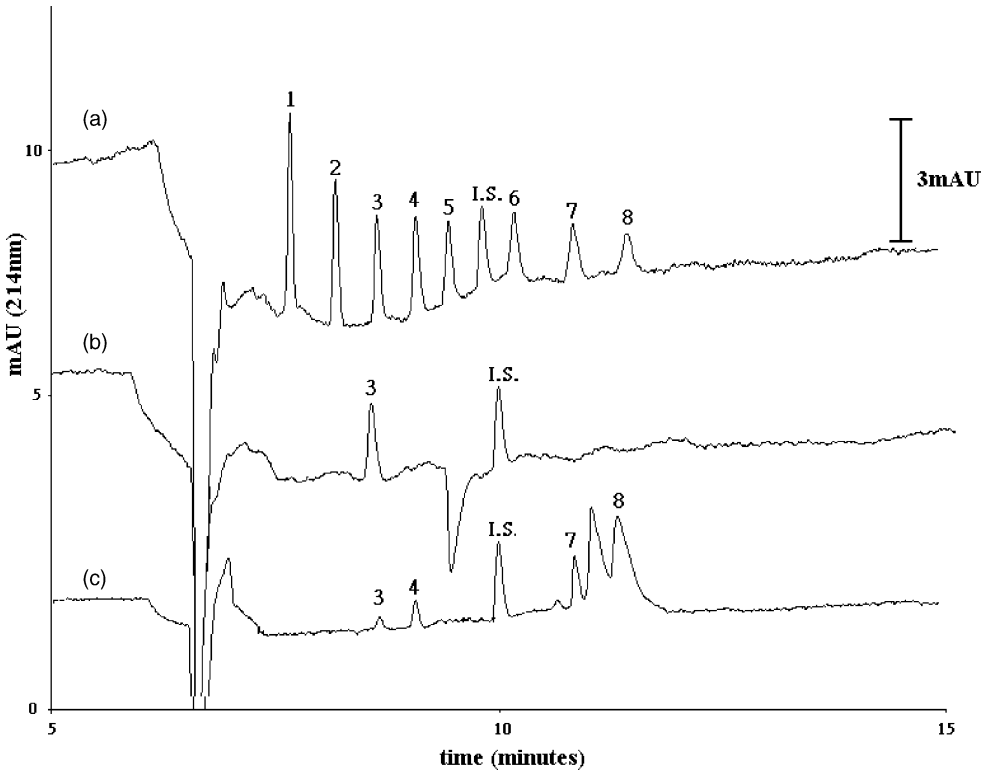

Fig. 5. Electropherograms for the separation of $ATMA^+$ and $DADMA^+$ homologues in commercial products: (a) standard mixture (5.0 μg/ml each of analyte), (b) hair conditioner-E, and (c) liquid fabric softener-D. Peak numbering and experimental conditions as given in Fig. 1, except THF content increased to 57.5%.

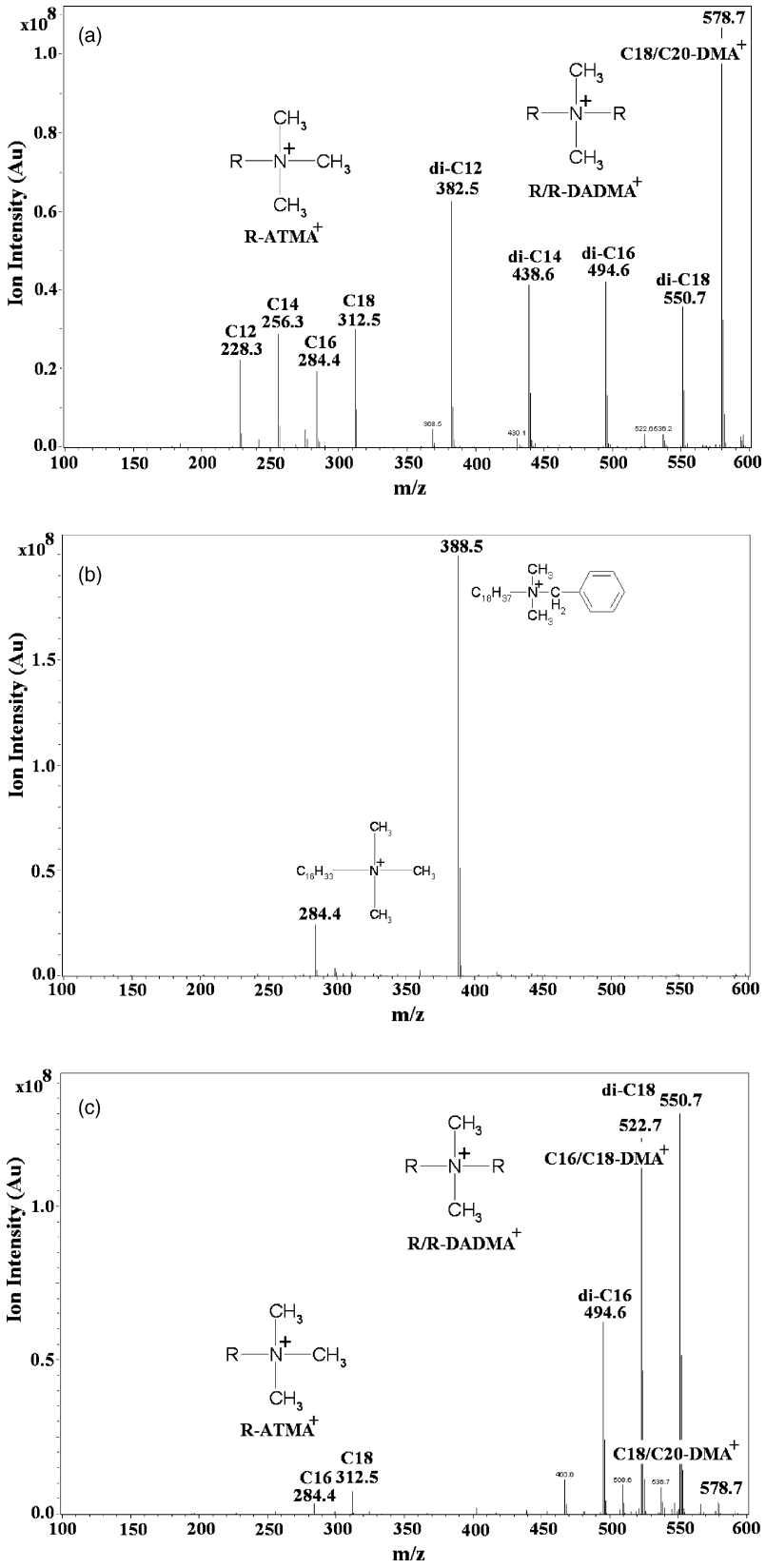

Fig. 6. ESI mass spectra of (a) standard mixture (1.0 μg/ml each of analyte), (b) hair conditioner-E, and (c) liquid fabric softener-D. Mass spectral conditions as given in Section 2.

of a mono-C_{16}/C_{18}-DMA^+ homologue in liquid fabric softener-D (Fig. 5c). However, quantitation was not calculated for this homologue due to the lack of the standard. Table 3 lists the contents of the di-C_{16}- and di-C_{18}-DMA^+ homologues in fabric softener-D, as estimated using peak heights.

4. Conclusion

The analytical procedure developed herein demonstrates that CE using indirect UV detection is a reliable and sensitive method, and offers a convenient analytical technique for determining non-chromophoric quaternary ammonium surfactants ($ATMA^+$ and $DADMA^+$ homologues) in hair conditioners and liquid fabric softeners. In separating these homologues by CE, organic solvent in sample solution, organic modifier (i.e., THF) content, buffer pH and the selection of chromophore are four important separation parameters which most affect the migration time and the resolution of $ATMA^+$ and $DADMA^+$ homologues. As expected, CE analysis leads to better peak shapes, higher efficiency and sensitivity, and consumes significantly less solvent than is required in HPLC analysis. The reproducibility of the migration time and the quantitative results of CE can be improved by internal standard. The results indicate that this CE method with indirect UV detection has the potential to become a more efficient and more useful method for non-chromophoric quaternary ammonium surfactants analysis, and can be applied to the quantitative analysis as well as qualitative analysis in commercial products of hair conditioners and liquid fabric softeners.

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