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Capillary electrophoretic analysis of the sodium salt of naphthalenesulfonic acid, formaldehyde polymer in waste water using a polyethylene glycol-coated capillary

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Abstract

Industrial surfactants such as the sodium salt of naphthalenesulfonic acid, formaldehyde polymer are widely used in manufacturing for process control. These water-soluble materials are eliminated with the waste water. This necessitates sensitive and accurate determinations of surfactant concentration in effluents as a prerequisite for effective pollution abatement. Monitoring the concentration of these surfactants by conventional spectrophotometric tests which are currently in use is non-differentiating and subject to gross interferences by many sources. Alternatively, determination of the above surfactant by HPLC methods has not been effective at resolving the various ionic species found. This work describes the selective separation of anionic species by the suppression of the EOF through the judicious choice of a commercially available coated column which increases selectivity by eliminating neutrals and cations through a bi-directional separation system. This is a significant enhancement over traditional approaches like HPLC which observe all UV-absorbing components and interferences. This selectivity is superior to that of the UV methods generating comparatively equivalent CE results when no interferences are present, and more accurate CE results when interferences are present.

1. Introduction

Emulsifiers have important widespread domestic and industrial applications. These materials are ultimately fated for treatment in waste water facilities. Accurate monitoring of these chemicals in pre-treated and post-treated effluents is essential for effective waste water processing. The specific determination of one complex anionic industrial emulsifier, the sodium salt of naphthalenesulfonic acid, formaldehyde polymer (NSA-FP) was previously performed by UV spectrophotometry [1]. The UV method was found to be non-specific for NSA-FP in the presence of other UV-absorbing chemicals which caused erroneously high results for NSA-FP. Other methods for the determination of anionic surfactants in effluents relied heavily on specific complexing of the anionic species with a fluorescent dye, rhodamine 6G, followed by fluorescence detection [2,3], or by reaction with methylene blue and colorimetric UV–Vis spectrophotometric detection [4–6]. These techniques can yield artificially high values because they lack the specificity required to monitor NSA-FP in the presence of other anionic surfactants and UV-

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absorbing chemicals. Additionally, HPLC procedures have been complicated due to the ionic character of these compounds [7–10]. These procedures lack either specificity, sufficient analyte resolution, or sensitivity.

While CE offers a viable alternative for the separation of anionic species, certain limitations must be considered when designing a separation strategy. The high electroosmotic flow inherent with a fused-silica CE technique could hinder the analysis of complex anions in solution by creating bulk fluid movement toward the injector side of the capillary column when a negative potential is applied (anode at the detector). A positive potential must be avoided if the goal of the experiment is to attract the anionic species past the detector window, since the anode is on the injector side of the column and the electrophoretic mobility of the anions will be toward the anode. The best way to solve this paradox of polarity-dependent mobility and EOF is by suppressing the EOF. Other works have described this EOF suppression or reversal by addition of modifiers such as quaternary ammonium salts and alcohols [11–14]. In the present work, free solution capillary electrophoresis (FSCE) is employed using a commercially available PEG-100 coated capillary column and buffer. The separation of anionic components is based purely on electrophoretic mobility of the analytes since the EOF is greatly suppressed. Unwanted neutral species and cations migrate toward the injector side of the column because of minimal EOF and reversed polarity, respectively. Since the anions migrate with strong mobility toward the detector side of the column, a bi-directional system exists. This bi-directional system provides a simplified process for separating and detecting the analytes of interest over traditional techniques like HPLC.

The UV test measures the absorbance of the effluents at 230 nm and a NSA-FP standard calibration curve is used for quantitation. However, this test has an unacceptable bias when interfering chemicals are present. Sample preparation steps for the UV test require filtration and dilution. No separation of NSA-FP analytes from other UV-absorbing species is attempted. Direct measurement of sample absorption versus a NSA-FP standard is the criterion for a positive result. The purpose of this FSCE methodology is the industrial process utilization of CE to replace a non-specific UV test. This study will explore the advantages of using FSCE in a simple approach to determine μg/ml levels of a commercial anionic surfactant. This paper presents a comparative study for the determination of NSA-FP in an industrial effluent system by CE and UV methods.

2. Experimental

2.1. CE experimental

The CE system used for this study was the Beckman P/ACE 5500 capillary electrophoresis instrument, equipped with a diode array detector (DAD) and System Gold software integration package (Beckman Instruments, Fullerton, CA, USA). A polyethylene glycol (PEG-100) coated capillary column 57 cm $\times$ 75 μm I.D. from Scientific Resources (SRI, Eatontown, NJ, USA) was employed to minimize the electroosmotic flow. The detector window was located 50 cm from the injection end of the capillary column. The CE electrical configuration was in reversed-polarity mode for anion detection (anode at the detector end) using a constant-current mode set at 30 μA (approximately 20 kV required).

New capillary columns were conditioned by rinsing with acetonitrile for 5 min, followed by a 5-min HPLC grade water rinse, and a 10-min rinse with the run buffer solution. A 3-min rinse of run buffer solution preceded and followed each sample and standard run.

The analysis run buffer solution was 40 m*M* sodium tetraborate, pH 9.0 (SRI, Eatontown, NJ, USA).

Pressure sampling was employed for 7 s using a pressure of 138 kPa to inject approximately 41 nl of sample or standard. This was followed by an injection of the sodium tetraborate electrolyte for 1 s at 138 kPa for a 6-nl buffer slug to eliminate diffusion of the sample into the injec-

tion run buffer vial. This sandwich technique significantly improved the precision of the test. The column was maintained at 18°C with the liquid cooling capability of the P/ACE system.

Detection for electropherograms was achieved at 228 nm with a 4-nm band width and was employed for all CE quantitative work. The DAD scanned in purity mode from 200 to 500 nm at a rate of 4 Hz, with the "scan on impurity" function activated. This function stores UV spectral data only when a component elutes with an adsorption within the scan range. This process was used to monitor for the presence of UV-absorbing materials not related to NSA-FP.

Samples were prepared by filtering a 1.0-ml sample aliquot with a 0.2-μm PTFE membrane (syringe type, Scientific Resources, Eatontown, NJ, USA). The filtrate was diluted to 4.4 ml by adding 1.0 ml of electrolyte solution, and 2.4 ml water. Quantitation was achieved with a five-point linear calibration curve of the emulsifier NSA-FP at a concentration range of 45 to 275 μg/ml. The calibration curve was generated by the response of NSA-FP at 228 nm (NSA-FP λ_{max}). The analysis time is 27 min.

2.2. UV–Vis experimental

The UV–Vis spectrophotometry testing was performed on a Beckman DU-70 UV–Vis spectrophotometer using a 1-cm cell path length at 230 nm. Samples were prepared by direct dilution with water at 1:200. Quantitation was achieved with a five-point linear calibration curve of the emulsifier NSA-FP at a concentration range of 0.7 to 5.5 μg/ml.

2.3. GC–MS experimental

Gas chromatography–mass spectrometry (GC–MS) support testing was performed on a Hewlett-Packard 5970B MSD GCMS system equipped with a 30 m × 0.25 mm I.D., 0.25 μm film thickness DB-5 MS capillary column (5% phenyl, 95% methyl, J&W Scientific, Houston, TX, USA). Samples were prepared by liquid–liquid extraction of 5 ml of sample with 0.5 ml of dichloromethane. The dichloromethane phase was isolated, concentrated to 100 μl, and a 1-μl aliquot was injected onto the GC–MS system. The GC capillary injection port was in the splitless mode for one minute at 240°C, and the column temperature program was as follows: 35°C for one minute, ramp at 8°C per minute to 300°C, hold at 300°C for 15 min. Helium pressure was held constant at 21 kPa. The mass spectrometer was scanned from 40 u to 700 u at 1.0 scan per second. The electron multiplier detector was maintained at 2400 eV; data was acquired on a HP Chemstation personal computer.

2.4. Reagents

All standard solutions were prepared by diluting 4 μg/ml stock solution containing the analyte, sodium salt of naphthalene sulfonic acid–formaldehyde polymer (Henkel Corp., Ambler, PA, USA). The NSA-FP is obtained as a 45% aqueous solution. Samples were prepared with 40 m*M* sodium tetraborate, pH 9.0 (Scientific Resources) and de-ionized water filtered by a HPLC grade water filtration system (Millipore, Bedford, MA, USA). Other interference reference materials were obtained as follows: sodium dimethyldithiocarbamate (Uniroyal Chemical, Middlebury, CT, USA); 2,6-bis-(1,1-dimethylethyl)-4-methylphenol (BHT: Aldrich, Milwaukee, WI, USA).

3. Results and discussion

3.1. Interferences eliminated

Prior to developing any electrophoretic separation, to accurately determine NSA-FP in effluents in the presence of neutral and ionic species, an understanding of the characterization of the undesired materials present in the effluents is required. Qualitative GC–MS was used as a support technique to identify neutral species present in the effluents which would interfere with the spectrophotometric test and would have to be resolved or screened by the CE. Some of

Table 1
Identification of neutrals present in effluents which could interfere with the UV test

Peak	Identification
1	Toluene
2	Phenol
3	N,N-Dimethyl methanthioamide
4	1,3-Dichlorobenzene
5	1-Phenylethanone (acetophenone)
6	4-Methylphenol
7	Alkylated phenols
8	Tetramethyl thiourea
9	1-Benzazine (quinoline)
10	2,3-Benzopyrrole (indole)
11	2,6-Bis-(1,1-dimethylethyl)-4-methylphenol (BHT)
12	1-Naphthalenol and 2-naphthalenol
13	Nonylphenol isomers
14	Alkylated benzothiophene
15	1,1-Sulfonylbis[4-chlorobenzene]
16	2,2'-Methylenebis[6-(1,1-dimethylethyl)-4-ethylphenol]

the UV-absorbing materials identified through the use of GC–MS are observed in Table 1. A total-ion chromatogram of a dichloromethane extract of industrial effluent is shown in Fig. 1. The N,N-dimethyl methanthioamide and tetramethylthiourea are secondary to the process effluent; their existence is due to the normal degradation of sodium dimethyldithiocarbamate (Na-DMDTC), as an anionic industrial process aid [15], which was present in the industrial effluents used in this study. The DMDTC anion is a strong UV absorber with approximately 30% of the extinction coefficient of NSA-FP at 230 nm. The presence of DMDTC introduces bias to the spectrophotometric test, generating erroneously high results for NSA-FP. To illustrate this bias, both a neutral and anionic species were specifically added to effluent at three different

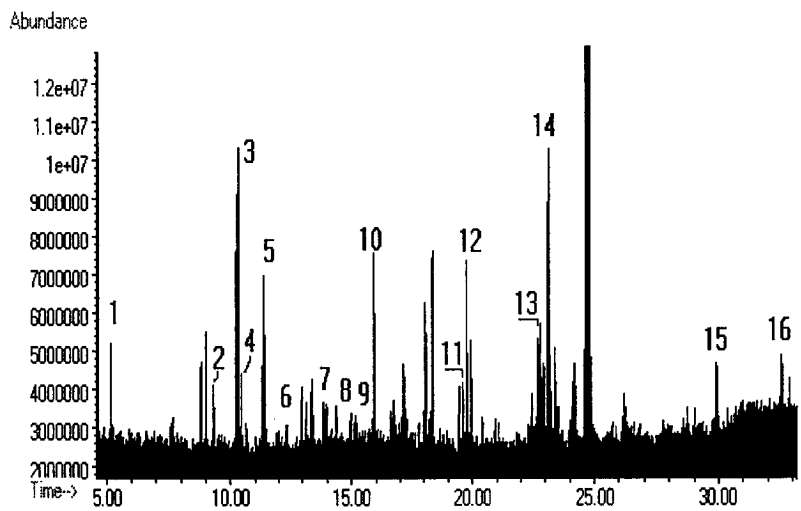

Fig. 1. GC–MS total-ion chromatogram of dichloromethane extract of industrial effluent. Components identified to be UV absorbers are identified in Table 1.

concentrations and analyzed by both UV and CE. The elimination of neutral species in the effluent is demonstrated by the addition of BHT (2,6-bis-[1,1-dimethylethyl]-4-methylphenol). A composite of six effluent samples was spiked with three levels of BHT. The composite was analyzed by CE and UV tests. The bias for NSA-FP values attributed to the spiked samples was significant for the UV test; negligible for the CE test. The DMDTC anion is readily separated and observed in the CE test. Thus, neutrals which bias the UV test are eliminated in the CE test, and anions which interfere with the UV test and are observed in the CE test are readily separated from the analyte of interest, NSA-FP. Table 2 shows both test results from spiking an effluent with an anion (Na-DMDTC) and a neutral species (BHT).

The elimination of neutral and cationic UV-interfering chemicals from the electrophoretic system by reversed polarity and minimal EOF accounts for the simple and accurate determination of the NSA-FP emulsifier by CE (Fig. 2). Neutral organics present in the waste water are not observed in the CE test since the EOF is extremely low due to the use of the polyethylene glycol coated capillary. Attempts to measure the EOF were not successful due to its extremely low value. A maximum EOF of 0.08 cm/min was calculated. Any EOF generated by the reversed

Table 2
Effects of spiking waste-water solution with Na-DMDTC and BHT

Amount added (μg/ml)	Found (μg/ml)	
	UV	CE
BHT		
0	0	0
1	1	0
10	4	0
100	38	3
Na-DMDTC		
0	0	0
402	99	6
1295	360	5
3687	1094	1

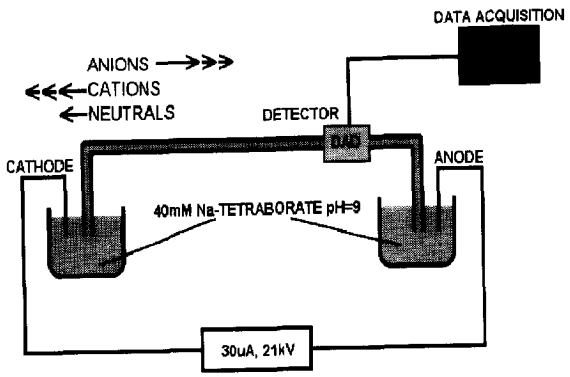

Fig. 2. Schematic diagram of the CE instrumentation used in this work. This configuration employs negative potential and a PEG-100 coated capillary column to eliminate EOF.

polarity mode is in the direction of the injector, causing neutrals to exit the capillary without passing the detector window. The reversed polarity is also responsible for the rapid migration of cations to the injector exit of the capillary column. Thus, only anionic species migrate through the coated capillary and are detected. Correlation of CE and UV results for the determination of NSA-FP in waste water effluents is generally good when no other UV-absorbing materials are present since both techniques monitor the NSA-FP when interferences are absent. The anionic materials present which were not related to NSA-FP were separated by the high resolving power of the FSCE. Fig. 3 shows the electrophoretic separation of DMDTC and NSA-FP.

The NSA-FP standard material is a complex, multiple component emulsifier. NSA-FP is a polymeric material with an average molecular mass of 2600 u. The generic structure for NSA-FP described in Fig. 4 is thought to contain an average of one sulfonic acid group (one negative charge) for each 220 u. Thus, the charge-to-mass ratio, which dictates the migration order of the analytes, tends to be constant for the bulk of the NSA-FP polymeric components. This constant-ratio theory is supported by the bulk of the NSA-FP components exhibiting the same electrophoretic mobility. Table 3 lists the electrophoretic mobilities of the NSA-FP and Na-DMDTC materials. The mobility values in Table

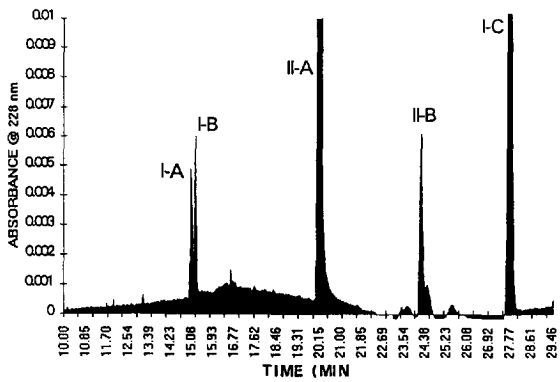

Fig. 3. Analysis of NSA-FP emulsifier in an industrial effluent with a Na-DMDTC spike resolved. Peak numbers refer to chemical structures in Fig. 4. Analytical conditions: capillary, fused-silica (PEG-100 coated 57 cm × 75 μm I.D.); electrolyte, 40 m*M* sodium tetraborate buffer (pH 9.0); constant current mode, 30 μA (approximately 21 kV applied); detection, UV absorbance at 228 nm.

3 are based on migration times and assume a zero electroosmotic flow. It should be noted that peaks I-A and I-B (Fig. 3) are indigenous to NSA-FP but exhibit different electrophoretic mobilities than the bulk of the NSA-FP constituents. The identity of peaks I-A and I-B is unknown; however, based on peak shapes, migration times, and pertinent chemistries it can be inferred than these two components are small-molecular-mass anions, perhaps inorganic sulfates. Peaks I-A and I-B are found in the standard NSA-FP, and are therefore not from the industrial effluent.

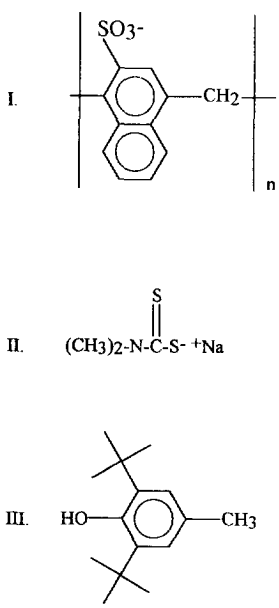

Fig. 4. List of the standards employed in this study: sodium salt of naphthalene sulfonic acid–formaldehyde polymer (I), sodium dimethyldithiocarbamate (II), and 2,6-bis-(1,1-dimethylethyl)-4-methylphenol (III).

3.2. Determination of NSA-FP

Fig. 5 shows the results of quantifying NSA-FP in an industrial effluent stream over time. When other compounds which absorb at similar wavelengths are present in the effluent, the UV results for NSA-FP are higher than the CE results. The results of the 30-day effluent study show an 8 percent lower average value for NSA-FP for CE compared to UV.

A three-level calibration curve with duplicate injections of standard NSA-FP was done daily. The standard calibration curve for NSA-FP was based on the peak area of the major NSA-FP peak (peak I-C, Fig. 3). Standard concentrations ranged from 30 to 250 μg/ml. Correlation coefficients of 0.9999 are typical using a least squares linear regression method. This method is rectilinear over the concentration range of interest (50–7000 μg/ml) and is sensitive to 50 μg/ml.

3.3. Repeatability and reproducibility

The calculations for repeatability (intra-day precision) and reproducibility (inter-day precision) were based on the assay values of a six-sample effluent composite. The initial concentration was diluted to make three samples; concentrations corresponded to the low (140 μg/ml), medium (250 μg/ml), and high (850 μg/ml) points of the calibration curve. This was accomplished using five replicates of each sample analyzed each day for three days. The CE test solutions were injected in duplicate and peak areas were averaged. Table 4 displays these statistical calculations for repeatability and reproducibility in %R.S.D.

The three-day average values (NSA-FP) for

Table 3
Electrophoretic mobility of NSA-FP and Na-DMDTC

Species	μ_{ep} ($cm^2\ min^{-1}\ V^{-1}$, $\times 10^3$)
Peak I-A (NSA-FP)	10.26
Peak I-B (NSA-FP)	10.08
Peak II-A (Na-DMDTC)	7.62
Peak II-B (Na-DMDTC degradent)	6.41
Peak I-C (NSA-FP, main component)	5.59

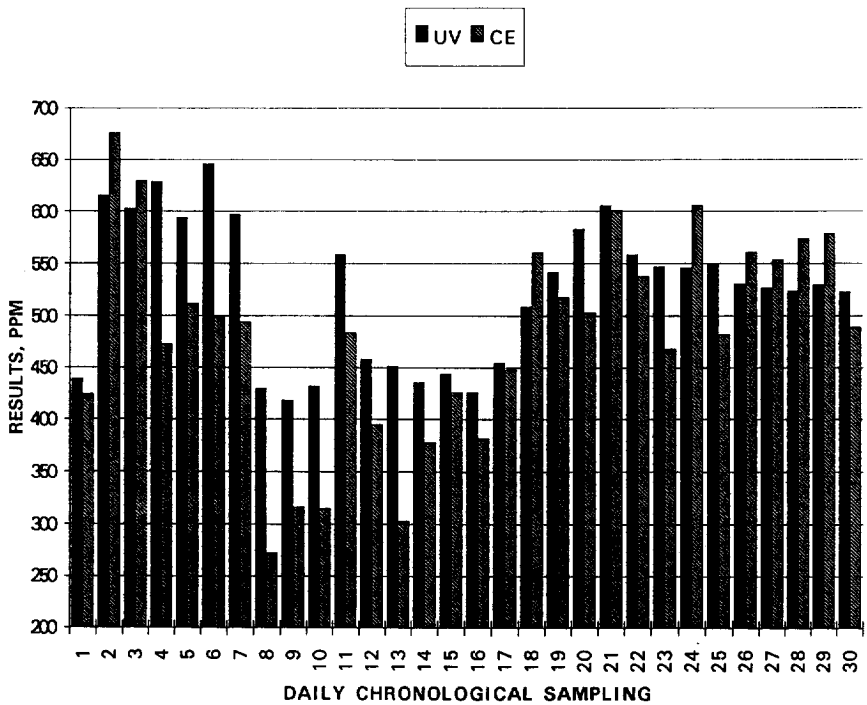

Fig. 5. Column chart displaying the comparison of CE vs. UV results for NSA-FP in industrial effluent samples collected over a 30-day period. CE values are significantly lower than UV values when other UV-absorbing chemicals are present. CE values were found to be an average of 8% lower than UV results for these samples.

Table 4
NSA-FP assay variability for CE and UV tests (in %R.S.D.)

Effluent dilution	Day 1		Day 2		Day 3		Inter-day	
	CE	UV	CE	UV	CE	UV	CE	UV
1:1	10.5	0.1	10.6	0.2	11.3	0.4	4.2	0.4
1:2	5.5	0.2	5.6	0.1	4.4	0.3	8.3	0.3
1:5	10.7	0.8	7.5	0.6	9.9	0.3	7.2	0.3

intra-day variability were found to be greater for CE than for the UV test by a factor of 22. The stability of the repeatability demonstrated by the UV test is partially attributed to the greater (1:200) dilution factor used in sample preparation, as opposed to 1:4.4 for the CE test. The UV test also demonstrated better reproducibility than the CE test by a factor of 20. The better precision of the UV test is offset by the better accuracy of the CE test. The values obtained for the three dilutions of the composite effluent were found to be 192, 104, and 42 μg/ml (or 22%, 41%, and 31%) greater for UV than CE for the 1:1, 1:2, and 1:5 dilutions, respectively. These higher values show the bias of the non-differentiating UV test.

4. Conclusions

Capillary electrophoresis using reversed polarity and coated column technology provides efficient, rapid, and accurate analysis of the surfactant, (sodium salt of) naphthalene sulfonic acid–formaldehyde polymer in waste water. Arduous sample preparations are not necessary, cations and neutral species do not interfere, and anionic chemicals are separated from the analyte. Results obtained by this method combine response from all polymeric analytes of interest while eliminating interfering chemicals. This method provides an increased level of confidence in the determination of NSA-FP in industrial effluents over existing spectrophotometric methodologies. The precision of the UV test is superior to that of the CE test for repeatability and reproducibility. Average relative standard deviations for both of these parameters were found to be 0.3% (UV) and 7.0% (CE). The CE test demonstrates greater accuracy than the UV test, estimated at 30% better based on comparative assays at three concentration levels for NSA-FP. The specificity of CE provides accurate data for the efficient control of pollution abatement procedures for municipal and industrial wastewater treatment facilities. The replacement of non-specific testing for the NSA-FP emulsifier in municipal and industrial effluents with capillary electrophoresis demonstrates the utility of the technique beyond the research laboratory environment.

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