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Short communication

Capillary zone electrophoretic separation of sulfonium and thiophenium ions

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Abstract

Capillary zone electrophoretic separation of sulfonium and thiophenium ions using phosphate buffer with TBA, pH 2.5, was investigated. Following their synthesis, 13 ions were synthesized and separated by this procedure. The benefits of speed and resolution has shown this method to be superior to that of conventional liquid chromatographic separation procedures. © 1998 Elsevier Science B.V.

Keywords: Sulphonium ions; Thiophenium ions; Sulfur compounds

1. Introduction

Sulfonium salts have been useful in the preparation of electrically conducting polymers, mechanistic enzyme studies and in the speciation of sulfur-containing components in petroleum [1–3]. There have been few articles published regarding the separation of these compounds and most have involved liquid chromatographic procedures such as ion-exchange, ion-pair and reversed-phase liquid chromatography [4–7]. To date, no work has been reported on the separation of this class of compounds by capillary electrophoresis (CE). Considering the increased speed and resolution provided by CE, a practical approach would be to investigate the usefulness of capillary zone electrophoresis in the separation of these ions.

2. Experimental

2.1. Chemicals and reagents

Phosphate buffer, pH 2.5, was purchased from Bio-Rad (Hercules, CA, USA). Tetrabutylammonium bromide (TBA), acetonitrile, dichloroethane and all sulfides, thiophenes and haloalkanes used in the synthesis of the ions were purchased from Aldrich and used without further purification. Silver tetrafluoroborate was purchased from Alfa Aesar (Ward Hill, MA, USA). Dichloroethane was dried over 4-Å sieves before use.

2.2. Instrumentation

A BioFocus Model 3000 capillary electrophoresis system from Bio-Rad equipped with a 45.4 cm (working length) × 75 μm I.D. fused-silica capillary column was used for separations. Sample introduction was achieved using the pressure mode set at 2 psi s (1 p.s.i. = 6894.76 Pa). Operation potential

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was fixed at 17 kV (60 μ A) normal mode at a column temperature of 15°C. The detection wavelength was fixed at 264 nm. The buffer was prepared by adding TBA directly to the standard 0.10 M phosphate buffer to attain a concentration of 50 mM. The buffer was then filtered through a 0.45- μ m membrane filter (Gelman Sciences) before use.

2.3. Synthesis of sulfonium ions

The procedure of Acheson and Harrison was used for the synthesis of the sulfonium and thiophenium salts [8]. Approximately 1 mmol of the corresponding sulfide and 1.2 mmol of the iodoalkane were dissolved in 2 ml of dry dichloroethane (DCE) in a 5-ml conical vial. A DCE solution of silver tetrafluoroborate (1.2 mmol AgBF₄ dissolved in 1 ml DCE) was added to this stirred solution and allowed to react for 2 h. The AgI was centrifuged and washed twice with 2 ml of acetonitrile. Solvents were removed by rotovaporization at 40°C. The salt was then dried under vacuum overnight at room temperature and used directly for CZE analysis. NMR was used as the analytical tool to verify existence of the sulfonium salt.

Stock solutions of sulfonium and thiophenium salts were prepared by dissolving 15 mg in 1.0 ml acetonitrile. The working standard was prepared by diluting the required amount of each stock solution with water–0.1 M phosphate buffer (50:50, v/v) to yield a final concentration of 2.5 mM. All working standards were filtered through a 0.45- μ m membrane filter before injection.

3. Results and discussion

A series of 13 ions were synthesized and are listed in Table 1. Capillary zone electrophoresis proved to be a good analytical tool for the separation of these compounds, as shown in Fig. 1. Table 2 lists selected sulfonium ions with their corresponding values of plate height (HETP) as an index of separation efficiency. As expected, the migration times of these compounds increased as the molecular mass increased with a few exceptions where substituent polarity/shape contribute to the separation process. Those compounds in the homologous series; A, C,

G, and K (alkylmethylphenylsulfonium) illustrate a logarithmic relationship between migration time and alkyl chain length. Under the described conditions the equation, $y=0.0306x+1.10$, where x =alkyl chain length and y =log(migration time (min)) was developed. This equation was generated using a linear least-squares fit routine and provided an r^2 value of 0.964. Migration time repeatability yielded a relative standard deviation of (R.S.D.) of 1.26% as determined by six repeated injections of compound C.

The use of TBA in phosphate buffer as the mobile phase, was effective and necessary in resolving the mixture of sulfonium ions. TBA is known to provide a significant capillary wall coverage which leads to a reduction or even a reversal of electroosmotic flow (EOF) at the acidic pH of 2.5 [9]. A series of experimental runs was performed varying the TBA concentration. Optimum resolution for this series of compounds was found to occur using a TBA concentration of 50 mM. At lower concentrations of TBA, 20 and 30 mM, resolution was dramatically decreased for all compounds.

The use of coated capillaries was not explored since effective resolution was achieved with the less expensive uncoated capillary. However, it is noted that an increase in efficiency might be expected by employing a coated capillary.

The use of CE for the separation of sulfonium ions appears to offer an improvement over established procedures. Massardier and Vialle reported on the investigation of liquid chromatographic systems for the separation of sulfonium salts [1]. In their study, they report results obtained from ion-exchange chromatography as well as ion-pair chromatography using C₁₈ packings and polymer packings. Their conclusions stated that the use of ion-pair chromatography with the polymer packing was superior due to decreased peak tailing which was experienced by the other procedures. However, for the limited number of compounds which were analyzed, poor resolution and very low retention volumes were obtained. For example, the reported retention volumes for diethylsulfonium, tetrahydrothiophenium and hexamethylene sulfonium were 1.3, 1.4 and 1.5 ml, respectively. Hoffman also reported an ion chromatographic procedure used for the separation of sulfonium ions and his results also indicated rela-

Table 1
Sulfonium and thiophenium ions

	Structure	Name	Molecular mass	Migration time (min)
A		Dimethylphenylsulfonium	139.29	13.16
B		S-methylbenzylthiophenium	149.2	13.47
C		Ethylmethylphenylsulfonium	153.26	14.42
D		Dimethyl-2-naphthylsulfonium	189.35	15.53
E		S-methyldibenzothiophenium	199.29	16.02
F		Methyl-diphenylsulfonium	201.31	17.10
G		Butylmethylphenylsulfonium	181.32	17.79
H		Benzylmethylphenylsulfonium	215.33	18.14
I		Benzylmethyl-p-tolylsulfonium	229.42	19.37
J		Dibenzylmethylsulfonium	229.42	19.70
K		Methyloctylphenylsulfonium	237.4	21.63
L		Methyl-di(4-methylbenzyl)sulfonium	257.48	23.06
M		Methyl-di(1-naphthyl)sulfonium	329.54	23.06

All compounds are BF_4 salts.

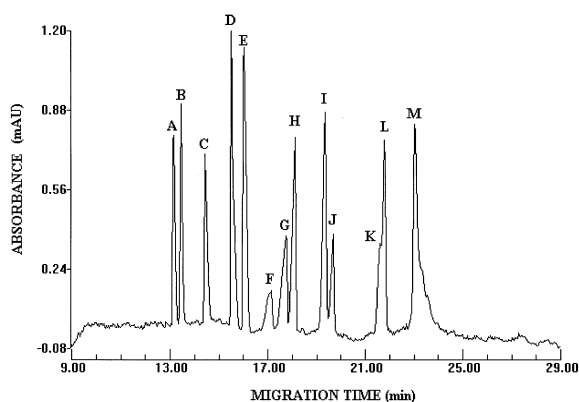


Fig. 1. Electropherogram of sulfonium and thiophenium ions.

tively limited resolution [2]. Recently, Howard and Russell reported a borohydride-coupled HPLC–flame photometric detection technique to determine dimethylsulfonium compounds [10]. Their work primarily emphasized the development of a new detection mode. However, the separation technique involved ion-exchange HPLC with cation-exchange being preferred over anion-exchange separation. They were able to separate a series of six sulfonium compounds within a run time of 20 min with satisfactory separation. Efficiencies were not reported.

Table 2
Index of efficiency for selected sulfonium ions

Compound	HETP (cm)
Dimethylphenylsulfonium	4.74×10^{-4}
Dimethyl-2-naphthylsulfonium	1.36×10^{-4}
S-Methyldibenzothiophenium	6.56×10^{-4}
Benzylmethyl- <i>p</i> -tolylsulfonium	4.81×10^{-4}
Methyldi(4-methylbenzyl)sulfonium	3.62×10^{-4}

In summary, CZE is shown to be an effective method for the analysis of sulfonium and thiophenium ions. This procedure offers the advantages of speed and higher efficiency over the commonly used ion-exchange liquid chromatographic methods. The technique should be useful in studies involved with these types of compounds. We are currently investigating enantioseparation of these compounds since many of them contain chiral sulfur centers.

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