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Speciation of organotin compounds by capillary electrophoresis using indirect ultraviolet absorbance detection

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Abstract

Capillary electrophoresis (CE) with indirect photometric detection was investigated for the separation of organotin species. Compounds such as dimethyltin (DMT), dibutyltin (DBT), and tributyltin (TBT) are important pollutants in the aqueous environment and techniques are needed to analyze directly aqueous environmental samples quickly and economically. By adjusting the mobile phase to pH 2.65 by HCl, tributyltin, dibutyltin and dimethyltin in aqueous solutions were separated by capillary electrophoresis using indirect ultraviolet (UV) absorbance detection. Pyridine was used as the UV absorption additive at 254 nm and separation was achieved in 6 min. Peak tailing obtained at higher pH suggests strong interaction between the dimethyltin cation and the negatively charged capillary wall. Cetyltrimethylammonium bromide (CTAB) was added to the mobile phase to improve the peak shapes when the pH of the mobile phase was greater than 3.5. Separations of organotin species in mobile phases with or without CTAB were compared. The change of electrophoretic mobility in mobile phases with different pH values indicates that DMT and DBT start to undergo hydrolysis at a pH 3.0. It was also found that the choice of the buffer anions is critical in the separation of the tin compounds as complexes appear to form with DMT and DBT in the presence of oxalate and citrate.

1. Introduction

Organotin compounds are a group of important pollutants in aqueous environments. These compounds, such as tributyltin, dibutyltin and dimethyltin, are widely used in many industrial, chemical and agricultural areas, as plastic stabilizers, fungicides, pesticides, and antifouling paints [1]. These compounds, when released into the environment, exhibit extreme toxicity to a wide range of aquatic organisms [2]. For example, it was proposed that the tributyltin contamination from antifouling paints was probably the cause of the sharp reduction of the oyster population on the Atlantic coast of France in 1980 [3]. The toxicity of organotin compounds is strongly dependent on the number and nature of the organic substituents [4]. It was found that triorganotin compounds are usually more toxic to aquatic organisms than the bi- or mono-organotins with the same substituents; tributyltin is the most toxic tin species in aqueous environments and has been widely used as a component in antifouling paints in maritime industry. Upon entering the aquatic environment, the organotin compounds can degrade into other organotin species [4]. Therefore, all these organotin species with their degradation products must be determined in order to investigate their environmental behavior and toxicity to aquatic ecosystems.

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So far, these compounds have been separated by gas chromatography [5], high-performance liquid chromatography [6] and supercritical fluid chromatography [7] employing a variety of specific detection systems, such as atomic absorption [8], atomic emission [9], flame photometric detection [10] and mass spectroscopy [6]. In most of these methods the organotin compounds need to be converted into their volatile derivatives first, followed by chromatographic separation. Usually the procedures are tedious and time consuming. Although the detectors are sophisticated and have high sensitivity, they can be costly and difficult to operate.

Electrophoresis is a well-established method in which ions are separated due to the difference in their migration rates under an external electric field. Capillary electrophoresis (CE), which uses narrow-bore capillary columns, is recognized as a powerful separation technique that separates, inexpensively and quickly, various biomolecules with high resolution and reproducibility. By proper selection of the mode of electrophoresis, inorganic and organic anions, cations, and neutral small molecules can be efficiently separated by this technique [11]. Most of the organotin species in aquatic environments exist as cations or electrically charged complexes [3]. Theoretically, although these organotin species can be separated by CE, only the analyses of organolead, organoselenium and organoarsenic compounds either by micellar electrokinetic chromatography (MEKC) [12] or by CE [13] have been reported. More recently the organomercury species were separated by CE [14]. In this paper we investigated the use of CE to separate organotin compounds in an aqueous solution. Compared with the traditional chromatographic techniques, the organotin species can be separated by CE without changing the actual chemical form of the species. The organotin compounds eluted from the outlet can be further studied in order to determine their real structures in the environment. In addition CE has the advantages of high speed, high efficiency, easy sample handling and relatively low cost.

At present UV absorption is the most important detection mode for CE. Direct UV absorbance detection, however, cannot be used to monitor the separation of organotin species because most of the organotin compounds do not contain a chromophore, although UV absorbance detection of the complexes formed between mono- or di-organotin species and complexing agents has been reported [15,16]. However, triorganotins, which are the most toxic group of organotin compounds, do not form stable complexes and cannot be monitored by direct UV absorbance detection. Indirect photometric detection (IPD) has become a simple and universal detection method for liquid chromatography and CE. In this method the non-absorbing ionic species are detected by changes in light absorption due to displacement of the absorbing co-ion [17,18]; thus indirect UV detection was used as a detection method for the CE separation of organotin compounds.

2. Experimental

A Waters (Milford, MA, USA) Quanta 4000 capillary electrophoresis system, which was supplied with both positive and negative high-voltage sources, was used. Fused-silica capillaries of 75 μm I.D. (60 cm total length, 53 cm from inlet to detector window) were obtained from Polymicro Technologies (Phoenix, AZ, USA). Indirect UV detection was conducted at 254 nm with the use of a mercury lamp and a 254-nm optical filter. Sample injection was either by hydrostatic or electromigration injection. The capillary was purged with 0.1 *M* NaOH (1 min), water (1 min) and the background electrolyte (2 min) between each run. The electropherograms were recorded by a SP-4270 integrator (Spectra-Physics, San Jose, CA, USA). For the convenience of integration, the positive and negative electrodes were switched so that the organotins eluted in the electropherograms as positive peaks.

Tributyltin chloride (TBT), dibutyltin dichloride (DBT), dimethyltin dichloride (DMT) and cetyltrimethylammonium bromide (CTAB) were obtained from Aldrich (Milwaukee, WI, USA). All the other chemicals used were of analytical

reagent grade. Because organotin compounds are hydrophobic, each organotin compound was first dissolved in pure methanol to give the 5 m*M* stock solutions. The standard solutions were freshly prepared by diluting the stock solution with water. Deionized and distilled water was used in all experiments.

The pH of the buffer solutions used in the CE system was adjusted by adding 2 *M* acid solutions of HCl, H_3PO_4, citric or oxalic acid. In order to avoid the presence of alkali metal ions in the mobile phase, no base solution (NaOH or KOH) was used to back-adjust the pH. All solutions were filtered with 0.22-μm filters and degassed before use.

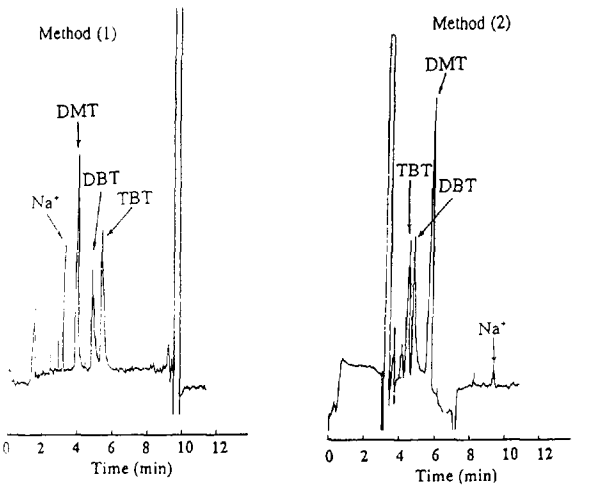

Fig. 1. CE separation of organotin compounds with different mobile phases. A 60 cm long capillary fused-silica column (75 μm I.D., 53 cm from the inlet to the detection window) was used and indirect UV detection at 254 nm for both methods. Method 1: mobile phase without CTAB. Method 2: mobile phase with CTAB. In both methods, DMT, DBT and TBT each 1.0 m*M*. For CE conditions see Table 1.

3. Results and discussion

We found that pyridine was a good UV-absorbing additive in CE cation separations. At $\lambda = 254$ nm the pyridium cation has both good sensitivity and a stable background. The optimum pH of the electrolyte was determined and the effect of electrolyte anions and the use of CTAB on the separation was investigated. By adjusting the background electrolyte containing 5 m*M* pyridine to pH 2.65 with HCl, complete separation of DMT, DBT and TBT was achieved in 6 min (Method 1 in Fig. 1). Electromigration injection was chosen to introduce the sample into the capillary because the detection limit was lower than with hydrostatic injection as a result of electrokinetic stacking. The first peak in the electropherogram was the H^+ peak. The Na^+ peaks in the electropherogram came from the 0.1 *M* NaOH purge solution which contaminated the sample through the electrode and capillary inlet.

3.1. Interaction between organotin compounds and the capillary wall

The adsorption of the organotin species on the silica stationary columns in liquid chromatography has been a problem. It was reported [6] that "the organotin compounds would not have eluted from the column without the addition of acetic acid". We encountered the same problem during the CE separation of organotins. It was found that with the mobile phase pH greater than 3.5, the peak of DMT tailed noticeably (Plot A of Fig. 2), while the TBT eluted sharply at the same condition. We speculate that there is strong interaction between the DMT cations and the negatively charged capillary wall whereas the interaction between TBT and the capillary is weak.

In order to prove our hypothesis, a home-made silica gel (60–80 mesh) column (80 × 1.3 mm I.D.) was used to preconcentrate DMT, DBT and TBT species in pure water followed by strong acid elution. It was found than DMT could be preconcentrated one hundred fold, DBT could be concentrated but to a lesser degree and TBT could not be enriched on the bare silica column.

The interaction between the various organotin species and the capillary wall can be explained by the structure of the organotin cations. TBT shows weak interaction with the negatively charged capillary surface because there are three large *n*-butyl groups covalently attached on the tin atom, making TBT +1 charged. Both the

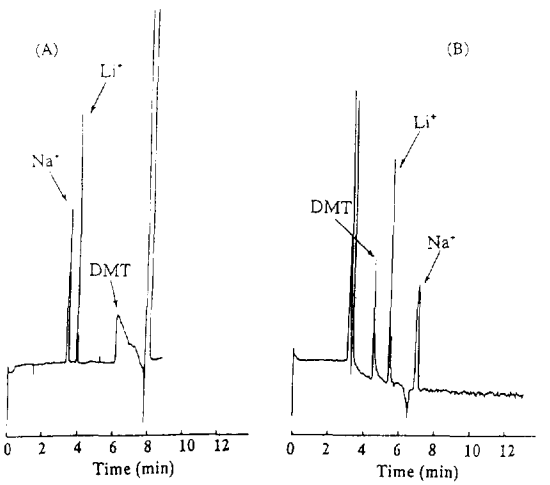

Fig. 2. Comparison of DMT peaks with different mobile phases. The same capillary and detection mode was used as in Fig. 1. Hydrostatic injection 20 s from 10 cm height was used in both methods. (A) Mobile phase contains 5 m*M* pyridine, pH adjusted to 4.00 by HCl; voltage, +20 kV. (B) Mobile phase contains 5 m*M* pyridine and 0.8 m*M* CTAB, pH adjusted to 4.00 by HCl; voltage, −20 kV.

steric hindrance and the +1 charge make the TBT cation less active. On the other hand, since there are only two small methyl groups around the tin atom in DMT, this cation has a +2 charge and is less sterically hindered; thus it could interact actively with the ionized silanol groups on the capillary. It has been reported [19] that when tributyltin in relatively high concentration ($C > 1.10$ mg/l) was stored in a Pyrex centrifuge tube, only a small amount of the TBT (less than 6%) adsorbed on the inner glass wall after 24 hour storage. However, the adsorption was greater than 67% when the concentration of TBT was decreased ($C < 0.24$ mg/l). The concentration of TBT used in our experiments (about 72.5 mg/l) was much higher than that in the reference so there was little adsorption, and the TBT peak eluted sharply. However, the adsorption of DMT on the negatively charged capillary wall was so strong that even at a relatively high concentration, the DMT still adsorbed strongly on the bared silica surface, resulting in poor peak shape.

To improve the peak shape of DMT when working at a pH greater than 3.5, CTAB at a concentration less than its critical micelle concentration (CMC) was added to the mobile phase. Since the cationic surfactant dynamically converted the capillary into a positively charged surface, the adsorption of the DMT cations was minimized or eliminated, and a sharp DMT peak was obtained (Plot B of Fig. 2). Therefore, a cationic surfactant such as CTAB can be used as an additive in the mobile phase to improve the peak shape in organotin speciation. Alternatively the poor peak shape of DMT can be improved by using a lower pH mobile phase to suppress the hydrolysis of the silanol groups in the capillary tubing.

3.2. Comparison of separation in the mobile phase with or without CTAB additive

The separation of DMT, DBT and TBT species in mobile phases with or without CTAB additives was compared (Fig. 1). The instrumental conditions of both methods are specified in Table 1. Positive voltage (anode at the injector end and cathode at the detector end) was used when no surfactant was present and a negative voltage (cathode at the injector end and anode at the detector end) with CTAB in the mobile phase (Table 1). When CTAB was added to the mobile phase, the surfactant changed the direction of the electroosmotic flow (EOF) and negative voltage had to be applied. The electropherogram shows that the order of elution was reversed, and TBT was detected first. This mode may be potentially useful in the fast screening of TBT in the field, provided that the detection method is sensitive enough for real sample analysis. TBT is the most important species in the organotin family.

For mobile phase without CTAB (Method 1), electromigration injection was chosen because the sample can be preconcentrated on-column and the detection limits reduced. It is interesting to see the amplification of the Na^+ peak by electromigration injection as compared with the hydrostatic injection. The sample cannot be preconcentrated by electromigration injection with the CTAB in the mobile phase (Method 2) because the electroosmosis and electrophoretic

Table 1
Conditions for CE of organotin compounds using different mobile phases

Mobile phase	Sample injection	Separation voltage (kV)	Current (μA)
Method 1			
5 m*M* pyridine, pH adjusted to 2.65 by HCl	10 kV electro-migration injection for 10 s	+20	22.4
Method 2			
5 m*M* pyridine and 0.8 m*M* CTAB, pH adjusted to 2.52 by HCl	10 cm hydrostatic injection for 20 s	−20	32.0

movements were in opposite directions; therefore if CTAB is in the mobile phase, hydrostatic injection was used. The effect of CTAB concentration in the mobile phase on the CE separation was also investigated. Results indicate that the separation efficiency increases with increasing CTAB concentration and reaches a plateau at about the critical micelle concentration (CMC), suggesting that the interaction between organotins and the capillary wall could be minimized as more surface is covered by CTAB molecules. At concentrations above the CMC, the separation of the organotin peaks was decreased with further increase of the CTAB. A possible explanation is that the poor separation is due to the increase in current and the formation of the positively charged micelles.

It was also found that at pH higher than 3, the peak of DBT was smaller and more poorly shaped with CTAB than without CTAB. We cannot explain this phenomenon as yet, but it appears that DBT is unstable in the mobile phase.

The reproducibility and the detection limits (DL) for both methods are shown in Table 2. The reproducibility of the retention time of the peaks is good both with and without CTAB, and the hydrostatic injection mode gave better peak area reproducibility than the electromigration mode.

However, CE separation using a mobile phase without CTAB (Method 1) is preferred because the detection limit can be decreased by electromigration stacking: the DBT decreased by 2.5-, the TBT by 3- and the DMT by 9-fold.

Micellar electrokinetic chromatography

Table 2
Reproducibility and detection limits of CE with different mobile phases

Compound	Reproducibility (%)		Detection limit (ppm)
	Retention time	Peak area	
Method 1 (without CTAB)			
DMT	0.3	1.5	1.3
DBT	0.4	8.1	11.2
TBT	0.5	5.7	9.9
Method 2 (with CTAB)			
DMT	0.3	2.6	11.6
DBT	0.2	4.1	28.6
TBT	0.3	3.5	30.5

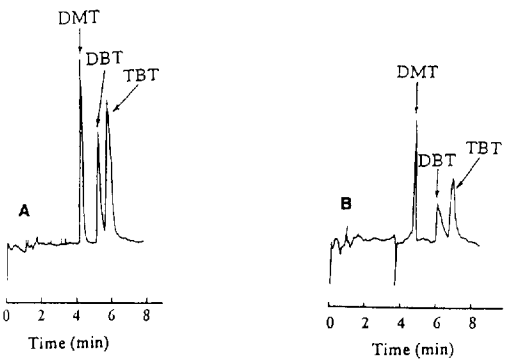

Fig. 3. Effect of Na^+ in the mobile phase on the organotin peak shape. (A) Mobile phase contains 5 m*M* pyridine, pH adjusted to 2.65 by HCl. (B) Mobile phase same as (A) plus 10 m*M* NaCl; voltage, +20 kV; hydrostatic injection 20 s from 10 cm height in both methods.

(MEKC) of organotin compounds with sodium dodecyl sulfate (SDS) was not investigated because of the restriction of the detection mode, even though separation of alkyltin compounds by SDS micellar liquid chromatography followed by ICP–MS detection has been reported [6]. It was found that a very small amount of Na^+ ion in the mobile phase could seriously reduce the sensitivity of the method since Na^+ competes with the UV-absorbing pyridium cation during the charge displacement process (Fig. 3). These results are similar to the results reported by Wang and Hartwick [20].

3.3. Hydrolysis of organotin compounds

We measured the migration time of DMT, DBT, TBT, Li^+, Na^+ and matrix peaks in mobile phases with and without CTAB additives, in a pH range from 2.75 to 4.50. The electrophoretic mobilities μ (which are the observed mobilities minus the electroosmosis mobility) of the organotin species and Na^+ and Li^+ were calculated.

Because the organotins were dissolved in methanol and water, the matrix showed as a big off-scale peak. For the CE runs in the mobile phase without CTAB, it was difficult to record the exact elution time of the matrix peaks to calculate the electroosmotic velocity. In order to reduce the relative error between each run, we recorded the time when the matrix peak just eluted as t_0, then used the equation

$$\mu = lL(1/t - 1/t_0)/V \quad (1)$$

to calculate the electrophoretic mobility μ of a solute in the mobile phase, where l and L are, respectively, the length of the capillary to detector and the total length of the capillary, V is the running voltage, t and t_0 are, respectively, the migration time of the solute and the matrix peak. The dependence of electrophoretic mobilities on the pH in the mobile phase without CTAB is shown in Plot A of Fig. 4.

When CTAB was added to the background electrolyte, the matrix peak eluted first. Several

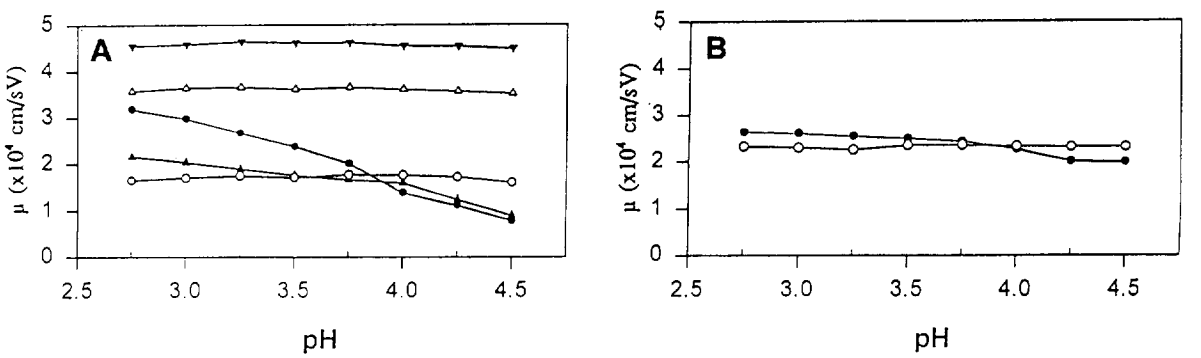

Fig. 4. Dependence of the electrophoretic mobilities of the solutes on the pH of the mobile phases: (A) without CTAB; (B) with 0.8 m*M* CTAB. Curves: ▼, Na^+; △, Li^+; ●, DMT; ▲, DBT; ○, TBT. CE conditions as outlined in Fig. 2.

sharp positive and negative peaks showed up in this neighborhood probably as a result of the refractive index change. It is difficult to decide which peak is the matrix peak and use its retention time as t_0 to calculate the electrophoretic mobilities of the solutes. From the calculation above it was found that the electrophoretic mobilities of Li^+ and Na^+ were stable over the pH range. The averaged value of μ_{Na} ($4.58 \cdot 10^{-4}$ cm^2/sV) and μ_{Li} ($3.61 \cdot 10^{-4}$ cm^2/sV) measured in our experiments seemed to be reasonable compared with the limiting values ($\mu_{Na} = 5.19 \cdot 10^{-4}$ cm^2/sV, $\mu_{Li} = 4.01 \cdot 10^{-4}$ cm^2/sV; $\mu_{Na} = 5.30 \cdot 10^{-4}$ cm^2/sV, $\mu_{Li} = 3.60 \cdot 10^{-4}$ cm^2/sV) reported [21,22]. We assume that the electrophoretic mobilities of Li^+ and Na^+ will not be affected by adding CTAB into the mobile phase and Na^+ and Li^+ were used as internal standards. The averaged value of μ_{Na} and μ_{Li} in the mobile phase without the CTAB additives were used to calculate the electrophoretic mobilities of DMT and DBT cations in the buffer with CTAB by the following equation:

$$\mu = 1/2[\mu_{Na} - lL(1/t - 1/t_{Na})/V + \mu_{Li} - lL(1/t - 1/t_{Li})/V] \quad (2)$$

where t_{Na} and t_{Li} are the migration time of, respectively, Na^+ and Li^+ peaks. The effect of pH on the electrophoretic mobilities of DMT and TBT in the mobile phase with CTAB is shown in Plot B of Fig. 4.

It is well known that during the electrophoresis process, a charged solute moves at its specific electrophoretic mobility μ determined by its electric charge q and size:

$$\mu = q/6\pi\eta r \quad (3)$$

where η is the medium viscosity and r is the hydrodynamic radius of the solute. For a weak acidic or basic ion, the change of the acidity of the mobile phase will interrupt its dissociation equilibrium, making it less or more charged. Accordingly the electrophoretic mobility of the solute will decrease or increase under the external electric field. Therefore, the electrophoretic mobility can be used as a tool to investigate the dissociation or hydrolysis equilibrium of the solutes in the buffer medium. Determination of the acid dissociation constants based on the electrophoretic mobility measurement has been reported [23].

As can be seen from Fig. 4, TBT behaves in a manner similar to Na^+ and Li^+: its electrophoretic mobility remains stable as the pH of the mobile phase changes. This behavior indicates that the TBT cation is stable from pH 2.75 to 4.5. However, the electrophoretic mobility of DMT without CTAB decreases rapidly when the pH increases, indicating that DMT hydrolyzes in a range of pH greater than 3. This hydrolysis hypothesis was also supported by the acid-base titration of 0.01 *M* dimethyltin dichloride water solution with NaOH solution (0.03 *M*). The initial pH of the DMT solution was 2.25 and the titration curve qualitatively agreed with the result of Tobias [24] that indicated that DMT undergoes a multi-step hydrolysis process in water solution.

The hydrolysis also appears to be closely related to the structure of organotin compounds. The organotin species, when dissolved in water, will first form simple aquo ions. Then the aquo ions hydrolyze by proton transfer from coordinated water molecules [25]. The two small methyl groups around tin in the DMT make it possible for the coordination of more water molecules. Therefore a proton transfer reaction can happen more easily in the DMT aquo ion than in the TBT ion. The dissociation constant of DMT ($pK_a < 3.5$) is reported to be larger than that of TBT ($6 < pK_a < 7$) [26] and supports our results obtained by comparison of the electrophoretic mobilities. It is obvious from Fig. 4 that the elution orders of these three organotin species changed when the pH of the mobile phase decreased, probably as a result of the difference of the hydrolytic properties of the organotin moieties.

When the pH decreases, the electrophoretic mobility of DMT increases more quickly in an unmodified capillary (no CTAB) than in the capillary that became positively charged when CTAB was added to the mobile phase. A possible explanation is that the mobility change in the negatively charged capillary column is a

combined effect of both hydrolysis and the adsorption of DMT cations on the capillary surface.

It can be seen from Fig. 4 that the electrophoretic mobility of TBT in different mobile phases was nearly parallel. At low pH value (pH < 3.75) the electrophoretic mobility of DMT decreased if CTAB was added to the mobile phase. Whether there is interaction between the hydrophobic organotin species and the positively charged surfactant with a hydrophobic tail needs to be studied in the future.

3.4. Interaction between organotin cations and the other anions in the mobile phase

The electropherograms of a mixture of DMT, DBT and TBT when different acids were used to adjust the pH of the mobile phase to 3.0 are shown in Fig. 5. Results suggest that complexes between diorganotins and buffer anions were formed. It has been reported [15] that the formation of complexes of mono- and di-organotin with oxine can be used to determine spectrophotometrically the organotin com-

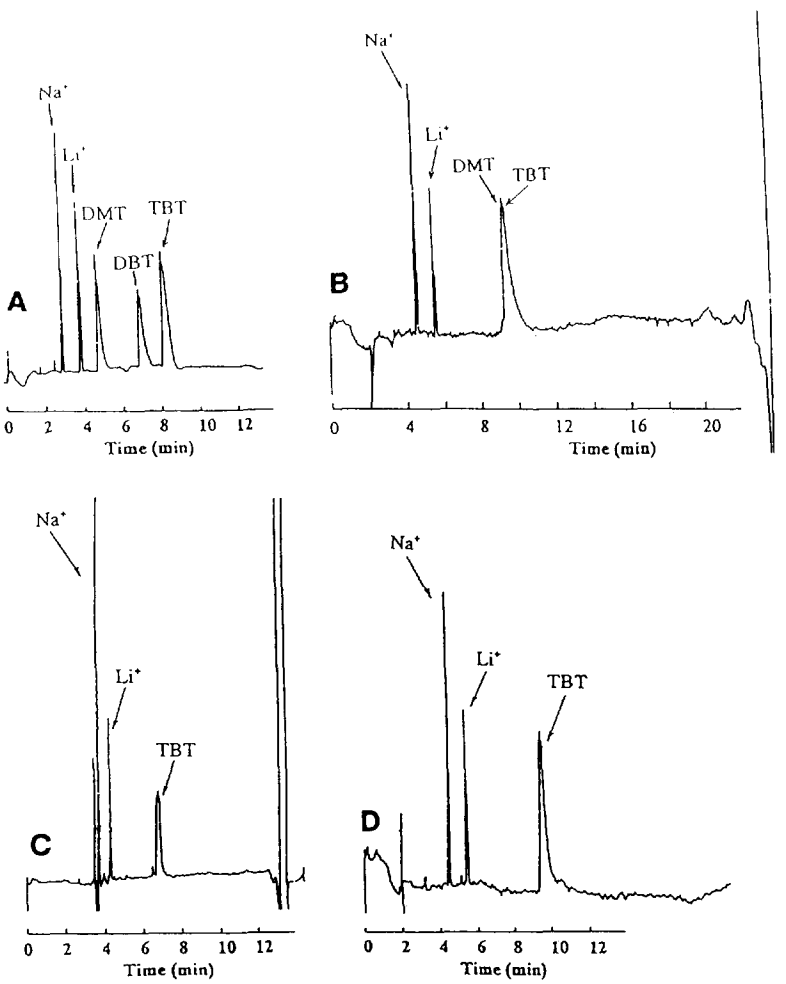

Fig. 5. Effect of different buffer anions on the separation of DMT, DBT, and TBT mixtures with Na^+ and Li^+ as the internal standards. The pH of the 5 m*M* pyridine electrolyte was adjusted to 3.00 by different acids. (A), HCl; (B), H_3PO_4; (C), oxalic acid; (D), citric acid. CE conditions as outlined in (A) of Fig. 2.

pounds. Mono- and di-organotin compounds form complexes easily because they are less sterically hindered than the triorganotins.

Based on the steric effect it appears that DMT should react more actively with complexing agents than DBT. However, there were no DBT peaks in the electropherograms when any of the mobile phases were used except HCl; however, the DMT peak also showed up in mobile phase with H_3PO_4. This suggests that other factors must be considered besides steric effects. The difference of the hydrophobicity between DMT and DBT may be one of the other factors. The reported [27] octanol–water partition coefficient (K_{ow}) of DBT (pK_{ow} about 1.5) is much higher than that of DMT (pK_{ow} about −3.2), indicating that DBT is more hydrophobic than DMT. Thus the DBT tends to form neutral complexes with other anions which either precipitate from the aquatic phase or co-elute with the matrix peak. Actually the method commonly used to preconcentrate organotin species before chromatographic separations involves the extraction into organic phases of the complexes formed between organotin species and the strong complexing agent, tropolone. Therefore strong complexing agents, such as tropolone and cyanide, were added to the sample and the mobile phase. The results showed that there were no peaks in the electropherogram for any of the organotin species.

4. Conclusions

Indirect UV absorbance detection proved to be useful in the CE separation of organotin species, when the UV-absorbing additive used was pyridine. The two factors that appear to influence the reactivity of organotin species are the steric effect and the hydrophobicity of the organic substituents. Electropherograms obtained with mobile phases of pH greater than 3.5 showed that the DMT peak tailed, indicating strong interaction between DMT and the bare capillary surface at a pH greater than 3.5. There are two ways of obtaining a good peak shape for DMT: working at a pH of less than 3 or coating capillary walls with CTAB at a pH greater than 3. The electrophoretic mobility as a function of buffer pH suggests that DMT and DBT hydrolyze at a pH greater than 3. Electropherograms obtained with different complexing agents indicate that the choice of the buffer anion is critical in the CE speciation of organotins. In addition, although DBT is believed to be a degradation product of TBT, our results suggest that TBT is more stable than either DMT or DBT.

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