



ELSEVIER

Journal of Chromatography A, 731 (1996) 299–303

JOURNAL OF
CHROMATOGRAPHY A

Migration behavior and separation of aromatic triazole and thiazole compounds by capillary zone electrophoresis

Ching-Erh Lin*, Chia-Chong Chen

Department of Chemistry, National Taiwan University, Taipei, Taiwan

Received 13 July 1995; revised 3 October 1995; accepted 3 October 1995

Abstract

The separation by capillary zone electrophoresis (CZE) of aromatic triazole and thiazole compounds, including benzotriazole (BTA), 5-tolyltriazole (5-TTA), dimethylbenzotriazole (DBTA), and 2-mercaptobenzothiazole (MBT), is described. These compounds, widely used as inhibitors of copper corrosion, were effectively separated using a fused-silica capillary with phytic acid (10 mM) as background electrolyte at pH above 8, except for pH of about 9.24 at which BTA and MBT migrate together. The migration behavior of these four analytes was investigated and their pK_a values were determined by CZE. This method was successfully applied to the analysis of a commercial product.

Keywords: Capillary electrophoresis; Corrosion; Triazoles; Corrosion inhibitors

1. Introduction

Aromatic triazole compounds, such as benzotriazole (BTA), 5-methyl-1H-benzotriazole or tolyltriazole (5-TTA), and dimethylbenzotriazole (DBTA), and aromatic thiazole compounds, such as 2-mercaptobenzothiazole (MBT) are well known to inhibit corrosion of copper alloys [1–3]. Several methods are reported to determine triazoles and MBT, including ultraviolet spectrophotometry [4], anodic chronopotentiometry [5], amperometric titration [6], and high-performance liquid chromatog-

raphy (HPLC) [1,7,8]. Until recently, HPLC was the only method capable of analyzing a mixture containing various triazoles and MBT [1,7].

Capillary electrophoresis (CE) has become a popular and powerful technique to separate diverse analytical samples [9–12]. This technique provides high resolution, great efficiency, rapid analysis and small consumption of solvent by comparison with HPLC. The development of this technique makes the separation of a mixture of ionic compounds an easy matter.

In this paper, a rapid capillary zone electrophoresis method is described to separate three aromatic triazole compounds and MBT. The migration behavior of these four analytes was investigated and their pK_a values were determined. The applicability

*Corresponding author.

of the developed method was demonstrated by the analysis of a commercial product.

2. Experimental

2.1. Chemicals

BTA, 5-TTA, DBTA, MBT, phytic acid, and dodecasodium salt of phytic acid (Aldrich, Milwaukee, WI, USA) were used as received. A commercial product, an automobile antifreeze (Toyota Company) received as gift from a local vendor, served as a sample.

A stock solution in methanol containing 1 mg/ml of each analyte was prepared. Mixed standard solutions were prepared by mixing a stock solution with adequate methanol to achieve the desired concentrations of standard solutions. Commercial sample used for CE analysis was diluted (1:400) with methanol.

2.2. Apparatus

Electrophoretic experiments were carried out on a Spectra-Physics Model 1000 capillary electrophoresis system (Fremont, CA, USA) with a capillary tube of fused-silica of 43 cm length and 50 μm I.D. Analytes were detected by on-column measurements of UV absorption at 200 nm at a position 36 cm from the injection end (anode) of the capillary. The CE system was interfaced with a microcomputer and printer with software CE1000 1.05A. A sample was injected in a hydrodynamic mode during 1 s. All CE experiments were performed at a constant temperature of 25°C. For pH measurements, a pH meter (Suntex Model SP-701) with accuracy of ± 0.01 pH unit was used.

2.3. Procedures

A new capillary column was washed for 60 min with NaOH (1.0 M) at 60°C, followed by 10 min with water at the same temperature and 10 min with water at 25°C. Before each injection, the capillary was flushed for 5 min with the buffer solution. The column was washed with NaOH (0.1 M) and water to return the electroosmotic flow (EOF) to normal when needed.

The buffer solutions were prepared by mixing stock solutions of phytic acid (100 mM) and dodecasodium salt of phytic acid (100 mM) at varied ratios and then adjusting to a total concentration of 10 mM with water. In this way, buffer solutions of desired pH were conveniently obtained.

All solutions were degassed by sonication and passed through a membrane filter (0.22 μm) before use. The electroosmotic mobility (μ_{eo}) was determined with methanol as neutral marker. The identification of analytes was performed by the spiking technique.

2.4. Calculations

Electrophoretic mobilities of solutes were calculated with the equation

$$\mu_{\text{ep}} = \mu - \mu_{\text{eo}} = \frac{L_t L_d}{V} \left(\frac{1}{t_m} - \frac{1}{t_{\text{eo}}} \right) \quad (1)$$

where μ_{ep} is the electrophoretic mobility of the solute tested, μ is the apparent mobility, μ_{eo} is the electroosmotic mobility, t_m is the migration time measured directly from the electropherogram, t_{eo} is the migration time for an uncharged solute (methanol as neutral marker), L_t is the total length of capillary, L_d is the length of capillary between injection and detection, and V is the applied voltage.

3. Results and discussion

3.1. Separation of aromatic triazoles and MBT

Phytic acid, used to improve the resolution in capillary electrophoresis [13], was selected as a background electrolyte. The use of phytic acid as a buffer has many advantages because this compound is almost transparent in the UV region at wavelengths greater than 200 nm; the current generated for phytic acid (10 mM) at pH 11.06 is only 41 μA at 20 kV. Furthermore, the polyanionic character of phytic acid renders it usable as a buffer over a wide pH range because its $\text{p}K_a$ values vary from 1.9 to 9.5 [14].

Three aromatic triazole compounds – DBTA, 5-TTA, and BTA – and a benzothiazole (MBT) which are widely used to inhibit copper corrosion were

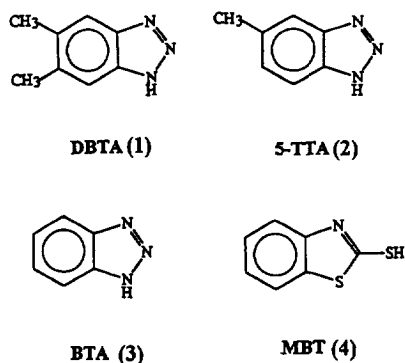


Fig. 1. Structures of three aromatic triazoles and MBT.

selected as analytes. Fig. 1 depicts the structures of these compounds. In Fig. 2, a three-dimensional spectral scan of CE separation of a mixture of four analytes is presented to show the characteristics of absorption spectra of these analytes. The optimum detection wavelength was set at 200 nm.

Fig. 3 shows electropherograms obtained for three triazoles and MBT using phytic acid (10 mM) as the running buffer at varied buffer pH. Complete separation of these four analytes was readily achieved within 4.5 min at an applied voltage of 20 kV and pH 11.06. The difference in mobility between 5-TTA and MBT at pH 11.06 was found to be $8 \cdot 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ which is larger than $6 \cdot 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the minimal difference of electrophoretic mobility to allow complete resolution for two consecutively migrating analytes with our CE system [15]. At this pH, electrophoretic mobilities of these four corrosion inhibitors follow the order DBTA < 5-TTA < BTA. Complete separation of all four analytes

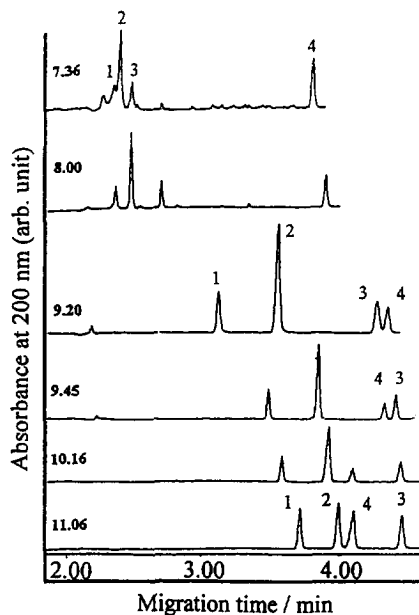


Fig. 3. Electropherograms of three aromatic triazoles and MBT at various buffer pH. Operating conditions as in Fig. 2.

was achieved in the pH range 7.80–11.06, except at about pH 9.24 at which BTA and MBT migrate together.

3.2. Migration behavior and migration order of aromatic triazoles and MBT

As shown in Fig. 4, the electrophoretic mobility of the three triazole compounds follows the order DBTA < 5-TTA < BTA in the pH range 7.36–11.06. The migration behavior of these triazoles is understandable, based on the differences in the ratio of charge to mass, because anions with a large ratio migrate more rapidly than those with a small ratio. Hence an anion with a greater negative value of electrophoretic mobility moves more slowly toward the cathode at which the detection window is located.

The migration behavior of MBT is somewhat different from that of triazole compounds. The electrophoretic mobility of MBT varies greatly in the pH range 6.0–8.0. At pH above 8.0, the deprotonated form of MBT becomes dominant and the mobility of MBT is almost invariant. The mobility of the anion form of MBT was found to be greater than that of

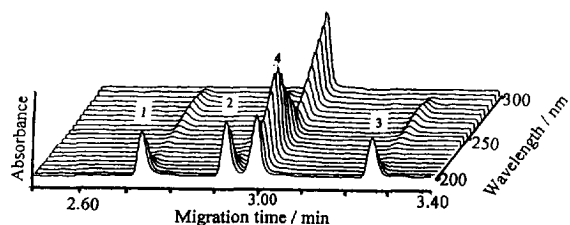


Fig. 2. Three-dimensional spectral scan of CE separation of a mixture of three aromatic triazoles and MBT. Buffer, 10 mM phytic acid; voltage, 20 kV; capillary, 43 cm \times 50 μm I.D. Peaks: 1=DBTA; 2=5-TTA; 3=BTA; 4=MBT.

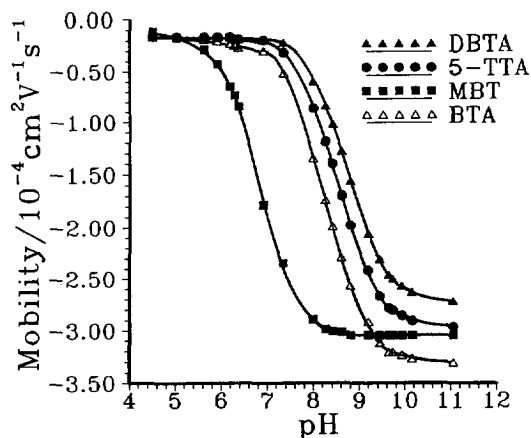


Fig. 4. Plots of effective electrophoretic mobilities of three aromatic triazoles and MBT as a function of pH. Operating conditions as in Fig. 2.

BTA but less than that of DBTA. At $\text{pH} < 9.24$, MBT migrated after BTA. At pH of about 9.24, MBT co-migrated with BTA, but at $\text{pH} > 9.24$ the migration order of these two analytes was reversed.

3.3. Determination of $\text{p}K_a$

Capillary zone electrophoresis is useful to determine the dissociation constants of acids [15,16] and bases [17]. With the aid of plots in Fig. 4, one can easily determine the $\text{p}K_a$ of each analyte which is a weak acid by estimating the best value of μ_{A^-} , the mobility of the fully deprotonated anionic form of each analyte at large pH ($> \text{p}K_a + 2$), of μ_{HA} , the limiting mobility of neutral triazoles, and then measuring the pH corresponding to $\mu_{\text{ep}} = 0.5(\mu_{\text{A}^-} - \mu_{\text{HA}})$ from the plot of μ_{ep} versus pH. Hence the $\text{p}K_a$ of each corrosion inhibitor is equal to the buffer pH at $\mu_{\text{ep}} = 0.5(\mu_{\text{A}^-} - \mu_{\text{HA}})$. Table 1 lists the values of $\text{p}K_a$ and μ_{A^-} determined for these four analytes.

Table 1
 $\text{p}K_a$ and μ_{A^-} values of copper corrosion inhibitors

Analytes	$\text{p}K_a$	μ_{A^-} ^a	μ_{HA} ^a
MBT	6.74	-3.04	-0.08
BTA	8.18	-3.31	-0.16
5-TTA	8.42	-2.98	-0.16
DBTA	8.63	-2.76	-0.16

^a Mobility in $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

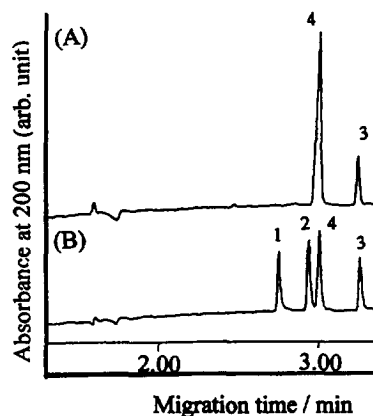


Fig. 5. Electropherograms obtained for a commercial product and a standard mixture. (A) Automobile antifreeze, and (B) standard mixture. Operating conditions as in Fig. 2, except that voltage is at 25 kV and pH at 11.06.

Since the experimental error in the determination of μ_{A^-} or μ_{HA} is $\pm 2.0 \cdot 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the precision of the $\text{p}K_a$ value determined by CZE is within ± 0.05 pH unit.

3.4. Analysis of commercial product

Typically, an automobile antifreeze is mainly composed of ethylene glycol [ca. 80–90% (w/w)], water [ca. 20–10% (w/w)], and a tiny amount of copper corrosion inhibitors. A commercial product was analyzed by CZE using a solution of dodecasodium salt of phytic acid (10 mM) at pH 11.06 as a running buffer. Fig. 5 shows the electropherograms obtained for this commercial sample and a standard mixture containing all four corrosion inhibitors for identification. Evidently, this automobile antifreeze contains both MBT and BTA.

For quantitative measurement, calibration curves for each corrosion inhibitor are required. DBTA was selected as an internal standard. To a solution (1.0 ml) of a sample at varied concentrations, DBTA solution (100 μl) of a fixed concentration was added, and the ratio of the peak height (R_{H}) of BTA or MBT to that of DBTA at varied concentrations was measured from the electropherogram. By plotting R_{H} values against inhibitor concentration, calibration curves for BTA and MBT were obtained.

The linearity of these two calibration curves are very good and the precision of R_H values is better than ± 0.015 . When the sample was diluted (1:400) with methanol, R_H (MBT) and R_H (BTA) values obtained were 0.417 and 0.087, respectively. According to these R_H values, the diluted sample contained 28 ppm MBT and 1.8 ppm BTA. This means the original sample contained 11.2 mg/ml MBT and 0.72 mg/ml BTA.

4. Conclusion

A rapid analytical method is developed to separate and to determine aromatic triazoles – BTA, 5-TTA and DBTA – and MBT by CZE. With dodecasodium salt of phytic acid (10 mM) as a background electrolyte and an applied voltage 25 kV, complete separation for these corrosion inhibitors was readily achieved within 4 min at $\text{pH} > 8.0$, except for pH of about 9.24 at which MBT and BTA migrate together. The method was successfully applied to the analysis of a commercial formulation.

Acknowledgments

We thank the National Science Council of the Republic of China for financial support.

References

- [1] T.M. Schmitt and E.S. Muzher, *Talanta*, 28 (1981) 777.
- [2] F. Mansfield and T. Smith, *Corrosion*, 29 (1973) 105.
- [3] H.D. Bennett, *Anal. Chem.*, 49 (1977) 322A.
- [4] M.H. Jones and J.T. Woodcock, *Anal. Chem.*, 47 (1975) 11.
- [5] J.D. Vorhines and J.S. Parsons, *Anal. Chem.*, 31 (1959) 516.
- [6] D.K. Basu and P.S. Bhattacharyya, *Anal. Chem.*, 48 (1976) 1602.
- [7] G.G. Hawn, P.A. Diehl and C.P. Tally, *J. Chromatogr., Sci.*, 19 (1981) 567.
- [8] A. Iob, F. Al-Yousef, B.S. Tawabini, A.I. Mohammed and N.M. Abbas, *J. Chromatogr. A*, 661 (1994) 245.
- [9] S.F.Y. Li, *Capillary Electrophoresis, Principles, Practice and Applications*, Elsevier, Amsterdam, 1992.
- [10] N.A. Guzman (Editor), *Capillary Electrophoresis Technology*, Marcel Dekker, New York, 1993.
- [11] P. Camilleri (Editor), *Capillary Electrophoresis: Theory and Practice*, CRC Press, Boca Raton, FL, 1993.
- [12] F. Foret, L. Krivonkova and P. Bocek, *Capillary Zone Electrophoresis*, VCH, Weinheim, Germany, 1993.
- [13] H.C. Birrell, P. Camilleri and G.N. Okafo, *J. Chem. Soc., Chem. Commun.*, (1994) 34.
- [14] W.J. Evans, E.J. McCourtney and R.J. Sharanger, *J. Am. Oil Chem. Soc.*, 59 (1982) 189.
- [15] C.E. Lin, W.C. Lin and W.C. Chiou, *J. Chromatogr. A*, 705 (1995) 325.
- [16] S.C. Smith and M.G. Khaledi, *Anal. Chem.*, 65 (1993) 193.
- [17] J. Cai, J.T. Smith and Z.E. Rassi, *J. High Resolut. Chromatogr.*, 15 (1992) 30.