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Why robust background electrolytes containing multivalent ionic species can fail in capillary zone electrophoresis

Jozef L. Beckers^a, Petr Gebauer^b, Petr Boček^{b,*}

^aDepartment of Chemistry (SPO), Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands

^bInstitute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, CZ-611 42 Brno, Czech Republic

Abstract

In this paper it is demonstrated that system peaks are induced by multivalent weak ionic species in background electrolytes. Their existence is derived from SystCharts and from Peak Shape Diagrams and the theory is confirmed experimentally. If analytes are present in a sample, with mobilities approximately equal to the mobility of a system peak, they interact, resulting in a strong increase of electromigration dispersion. This leads to strong peak broadening, peak deformation and a loss of resolution. Typical background electrolytes containing multivalent ionic species, e.g. phosphate and phthalate buffers, often reported to be robust electrolytes, are therefore not always universally applicable and can fail for the application of specific analytes. This paper reports a systematic study of the above phenomena and shows both theoretical and experimental results for background electrolytes containing phosphoric acid and phthalic acid. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Background electrolyte composition; Peak shapes; System peaks; Capillary electrophoresis; Organic acids

1. Introduction

During the last few years it has become more and more clear that system peaks (SPs), i.e. peaks which do not contain any of the sample components, do exist and migrate through electrophoretic separation chambers with a mobility determined by the composition of the background electrolyte (BGE) [1–4]. If the mobilities of sample components are close to the mobility of a SP, there is a strong interaction between the sample component and the SP resulting in peak deformation [5,6] due to the so-called schizophrenic broadening [7,8]. Generally, a strong electromigration dispersion (EMD) occurs, resulting

in broad peaks through which the resolution strongly decreases. Applying BGEs consisting of n ionic species (both anionic and cationic species have to be counted), $n - 1$ SPs are present in the electropherograms. These SPs include in addition to one non-moving electroosmotic flow (EOF) peak, $n - 2$ moving SPs [9]. For a BGE consisting of a single anionic and a single cationic species ($n = 2$) only one EOF peak will be present. Applying a BGE with two co-ionic species ($n = 3$), an EOF peak and a moving SP can be expected. The mobility of the SP lies between the mobilities of the two co-ionic species. For BGEs at very high or low pH, the hydroxyl or hydrogen ions act as a second co-ion and this will cause SPs [2,10].

Multivalent ionic species migrate as a single sample peak in electrophoresis and are considered as a single ionic species. Recently, it was shown that, in

*Corresponding author. Tel.: +420-5-4163-6183; fax: +420-5-4121-2113.

E-mail address: bocek@iach.cz (P. Boček).

BGEs consisting of only two ionic species ($n = 2$), containing, however, a multivalent weak ionic species, a SP can be present [11,12]. BGEs consisting of multivalent ionic species are often applied for the analyses of diverse components in diverse matrices and in the literature they are often presented as robust, universally applicable electrolyte systems. Examples are diverse BGEs containing phosphoric acid and phthalic acid. If SPs can be present here, they can deform sample component peaks and this means that such BGEs can fail for the analysis of these components and are not universally applicable.

In this paper we will first consider how the existence of SPs can be revealed and some examples will be given of visible SPs and their effect on separations. Further, the presence of SPs when applying BGEs containing multivalent ionic species will be discussed and the influence on separations when applying some well-known BGEs will be shown.

2. Experimental

2.1. Instrumentation

For the CZE experiments, a P/ACE System 2000 HPCE (Beckman, Fullerton, CA, USA) was used. With this apparatus, experiments were carried out applying two Beckman eCAP capillary tubings (75 μm I.D.) with total lengths of 46.7 cm and 40.0 cm and distances between injection and detection of 57.1 cm and 50.3 cm, respectively. The wavelength of the UV detector was set at 214 nm and the experiments were carried out applying a constant voltage of 15 kV. If the anode was set at the outlet, cetyltrimethylammonium bromide (CTAB) was added to the BGE used in order to have anodic EOF. The operating temperature was 25°C and sample introduction was performed applying pressure injection of $3.4 \cdot 10^3$ Pa for 3 s, unless otherwise specified. Data analysis was performed using the laboratory-written data analysis program CAESAR.

2.2. Chemicals

All chemicals were of analytical-reagent grade. Deionized water was used for the preparation of all

buffer and sample solutions. For the preparation of BGEs at high pH the water was boiled in order to remove carbon dioxide. Standard solutions of anionic species serving as model samples were prepared by dissolving, respectively: sodium salts of acetate, formate and citrate; free acids for tartrate, mandelate, trichloroacetate, pyrazol-2,3-dicarboxylate, hippurate, salicylate, phthalate and picrate; and equimolar mixtures of slightly soluble free acids and Tris for succinate, caproate, maleate and butyrate.

3. Results and discussion

System peaks can be defined as BGE-like zones, i.e. as zones which do not contain any sample component. They consist of ionic species of the BGE, although at a concentration and pH deviating from those of the BGE. The best-known SP is the EOF dip/peak, a zone in the electrophoretic system where the BGE has a different concentration locally because it is adapted to the omega value of the original injected sample solution according to the regulating function of Kohlrausch (KRF) [13]. This EOF peak moves with the speed of the EOF. Other SPs have their own electrophoretic mobilities and migrate at different speeds.

3.1. How the existence of SPs can be predicted

The existence of system peaks in electrophoretic processes can be predicted by applying so-called SystCharts [14] and Peak Shape Diagrams (PSDs) [15] and both methods are based on calculations with a mathematical model. For a good comparison of the two mathematical models, all mathematical equations are extended for the application of multivalent components, and in order to avoid deviations by differences in corrections, no corrections are applied for activities or for electrophoretic effects according to Debye, Huckel and Onsager. If calculated values for the mobilities obtained in this way are compared with experimentally obtained mobilities, they should be corrected [16].

The mathematical model which forms the background of the SystCharts has been described previously [14] and with this model all parameters in the electrophoretic zones of sample components can be

calculated. A SystChart consists of eight panels in which the relationships between the most important parameters in a sample zone, including the pH, the concentrations of co-ions and counter ionic species and the quotient E_1m_1/E_2m_2 , are visualized versus the mobilities of anionic and cationic sample species for a given BGE. The ratio E_1m_1/E_2m_2 describes the peak shape and is the quotient of the velocities of a sample component in the BGE and in its own zone, calculated for a sample zone at 0.0005 M and for strong anionic species. If this ratio is larger than unity the peak is fronting, if it equals unity the peak is symmetric and values below unity represent tailing peaks. This panel of the SystChart is used in the comparison with PSDs. It has been demonstrated that discontinuities in the relationships indicate the existence and mobilities of a SP. Sometimes the mobilities of SPs can be calculated directly [1].

In PSDs [15] the relationships between the slopes S of the velocities of sample zones versus anionic mobilities of the sample components are represented for diverse pK values. For a negative value of S , fronting peaks, and for positive values tailing peaks, are obtained. At a specific mobility, the slope changes from a negative to a positive value (contour of symmetry, $S = 0$), i.e. peak shapes change from a fronting to a tailing character. If a PSD contains two contours of symmetry then the values of the slope S exhibit a discontinuity between these contours of symmetry and reveal the existence of a SP. In fact, this is a discontinuity comparable to those that can be observed in SystCharts.

As an example of these methods and to compare both methods, Figs. 1 and 2 show the panel E_1m_1/E_2m_2 of the SystChart and the PSD for a BGE consisting of a mixture of 0.005 M formic acid, 0.005 M salicylic acid and 0.02 M Tris at pH 8.1. Table 1 shows all mobilities at infinite dilution and pK values for ionic species used in the calculations and experiments. From Fig. 1 it can be observed that two points of symmetry are present, where the fronting character changes to a tailing character. If the ratio E_1m_1/E_2m_2 is larger than 1, fronting zones are obtained, otherwise tailing zones, and the changes take place at the mobilities of the two co-ionic species, viz. formic acid ($-56.6 \cdot 10^{-9} \text{ m}^2/\text{V s}$) and salicylic acid ($-35.4 \cdot 10^{-9} \text{ m}^2/\text{V s}$). Between these points of symmetry there must be a

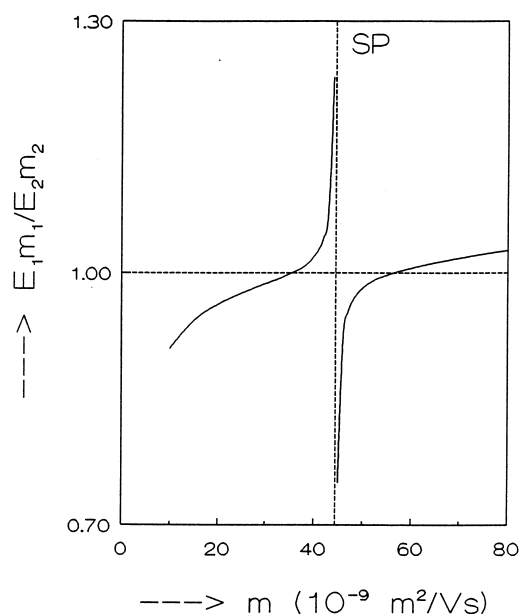


Fig. 1. Calculated relationship between E_1m_1/E_2m_2 and anionic mobility of sample ions applying a BGE consisting of 0.005 M formic acid, 0.005 M salicylic acid and 0.02 M Tris at pH 8.1. The position of the discontinuity, the vertical dotted line, in the relationship indicates the existence of a SP with a mobility of ca. $-44.5 \cdot 10^{-9} \text{ m}^2/\text{V s}$. For further information, see text.

discontinuity indicating the existence of a SP with a mobility of $-44.5 \cdot 10^{-9} \text{ m}^2/\text{V s}$. In Fig. 2 the PSD is given for the same BGE. In this diagram the

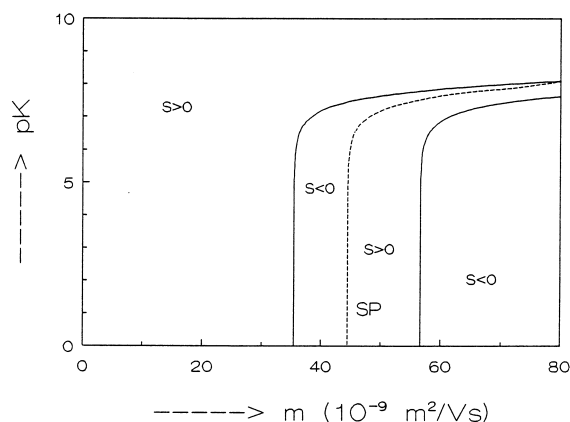


Fig. 2. Peak Shape Diagram for the same BGE at pH 8.1 as used in Fig. 1. Two contours of symmetry ($S = 0$, —) are visible and between them there is a discontinuity present ($\cdot \cdot \cdot$) representing the existence and mobility of a SP. For further information, see text.

Table 1
Mobilities at infinite dilution, m ($10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$), and pK values for ionic species used in the simulations and experiments

Ionic species	m	pK
Acetic acid	-42.4	4.76
Caproic acid	-30.2	4.857
Carbonic acid	-46.1	6.352
	-71.8	10.329
Citric acid	-28.7	3.128
	-54.7	4.761
	-74.4	6.396
Formic acid	-56.6	3.752
Hippuric acid	-25.3	2.70
	-55.1	7.271
Hydrochloric acid	-79.1	-2.0
Iodic acid	-42.0	0.77
Maleic acid	-41.3	1.921
	-62.4	6.225
Mandelic acid	-28.3	3.411
Nitric acid	-74.1	-1.73
Phosphoric acid	-35.1	2.12
	-61.5	7.21
	-71.5	12.67
Phthalic acid	-28.1	2.89
	-52.9	5.10
Picric acid	-31.5	0.708
Pyrazol-2,3-dicarboxylic acid	-33.8	1.000
	-56.0	4.228
Salicylic acid	-35.4	3.107
Sodium	51.9	14.0
Succinic acid	-33.0	4.207
	-60.9	5.638
Tartaric acid	-32.6	3.036
	-60.7	4.366
Potassium	76.2	14.0
Trichloroacetic acid	-37.9	0.635
Tris	29.5	8.1

regions are given for positive and negative values of the slopes of the velocities of the sample zones (S , defined as dv/dc) and the boundaries between these regions, with $S = 0$ (full lines), indicate the points of symmetry versus the mobilities of the sample ions for varying pK values. For strong anionic species (see $pK = 0$) the points of symmetry lie at the mobilities of the co-ionic species formic acid and salicylic acid, just as in Fig. 1. The discontinuity (dotted line) gives, for the system peak, a mobility of $-44.5 \cdot 10^{-9} \text{ m}^2/\text{V s}$, the same value as obtained from the SystChart. In order to demonstrate this behaviour, Fig. 3 shows the measured electropherogram

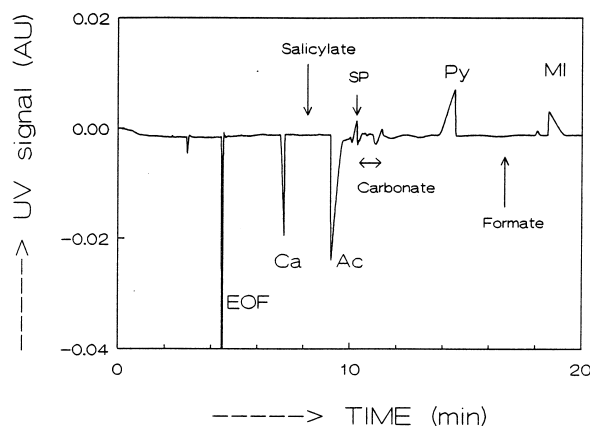


Fig. 3. Measured electropherogram for injection of a mixture of 0.001 M caproate (Ca), acetate (Ac), pyrazol-2,3-dicarboxylate (Py) and maleate (MI). The position of the centres of symmetry and the SP are indicated by arrows. The region of disturbances caused by the presence of carbonate is depicted by a double arrow.

ram for the separation of a sample consisting of $1 \cdot 10^{-3} \text{ M}$ caproate, acetate, pyrazol-2,3-dicarboxylate and maleate applying the BGE used in Figs. 1 and 2. The experiment was carried out in the cathodic mode (cathode at the outlet) and with capillary tubing of total length 57.1 cm. First the EOF peak can be observed and then the negative ionic species. Clearly, it can be seen that maleate, the most mobile ionic species, is fronting and pyrazol-2,3-dicarboxylate, with a mobility slower than that of formate (position indicated by an arrow), is tailing. There exists a point of symmetry between these ionic species. Both components are visible as peaks, because these ionic species are UV absorbing. Acetate and caproate are visible as dips, because they are non-UV absorbing and are measured in the indirect UV mode. It is remarkable that acetate is fronting and caproate is tailing, indicating that there is a second point of symmetry. It is clear that there must be a system peak with a mobility just higher than that of acetate, marked by an arrow. In front of the SP the baseline is not stable. In the first instance this baseline was bad due to the presence of carbon dioxide in the water giving bicarbonate in the BGE at pH 8.1, with a mobility of ca. $46 \cdot 10^{-9} \text{ m}^2/\text{V s}$. This disturbance was smaller after boiling the distilled water before use. We also tested anodic migration with anodic EOF in the presence of CTAB.

However, we did not obtain stable baselines, probably due to the combination of high pH and CTAB.

3.2. BGE consisting of multivalent ionic species

Multivalent ionic species, such as phosphoric acid and phthalic acid, generally behave like a uniform substance and migrate as a “single zone” with an effective mobility determined by all ionic mobilities of all forms of the component. Recently, Gebauer et al. [11,12] deduced the existence of SPs by applying BGEs consisting of multivalent ionic species in phosphate systems from PSDs and observed peak deformations due to this SP. This seems to indicate that BGEs consisting of multivalent ionic species themselves behave as BGEs containing more co-ions. Because in phosphate systems the SPs are not visible as the BGE is non-UV absorbing, we applied phthalic acid, a bivalent anionic species which has UV absorbing properties, in order to investigate the behavior of multivalent ionic species. In the first instance, we calculated the SystChart and the PSD for a BGE consisting of 0.005 M phthalic acid and 0.0075 M Tris at pH 5.1. Fig. 4 shows the relationship between E_1m_1/E_2m_2 and the anionic mobility of sample ions from the SystChart, and Fig. 5 shows the PSD for this BGE. Two contours of symmetry can be observed, both in the SystChart and in the PSD, at mobilities of ca. -53 and $-27 \cdot 10^{-9} \text{ m}^2/\text{V s}$ and these values are comparable to the ionic mobilities of the divalent and monovalent ions of phthalic acid. Furthermore, the existence of a SP with a mobility of ca. $-31 \cdot 10^{-9} \text{ m}^2/\text{V s}$ can be deduced from the discontinuities in SystChart and PSD. To check the foregoing experimentally, experiments were carried out for the separation of a selected series of anionic species in a BGE of 0.005 M phthalic acid and 0.0075 M Tris at pH 5.1. Fig. 6 shows measured electropherograms for injections of 0.001 M solutions of (a) caproate, (b) mandelate, (c) formate and (d) nitrate applying a BGE of Tris phthalate at pH 5.1. CTAB was added to the BGE in order to achieve anodic EOF and the anode was set at the outlet. In all electropherograms, three SPs could be observed. One of EOF, a SP with a measured mobility of ca. $-70 \cdot 10^{-9} \text{ m}^2/\text{V s}$ caused by the presence of bromide in the BGE and a SP with an average measured mobility of ca. $-26.5 \cdot 10^{-9} \text{ m}^2/\text{V s}$ caused by the

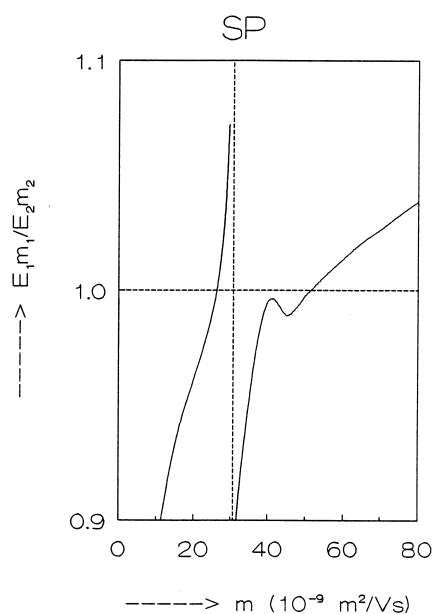


Fig. 4. Calculated relationship between E_1m_1/E_2m_2 and mobility of sample anionic species on applying a BGE consisting of 0.005 M phthalic acid and 0.0075 M Tris at pH 5.1. The discontinuity at a mobility of ca. $-31 \cdot 10^{-9} \text{ m}^2/\text{V s}$ indicates the existence of a SP.

presence of the bivalent phthalic acid in the BGE. The measured mobility of $-26.5 \cdot 10^{-9} \text{ m}^2/\text{V s}$ corresponds quite well with the mobility of the SP of $-31 \cdot 10^{-9} \text{ m}^2/\text{V s}$ calculated without any correction.

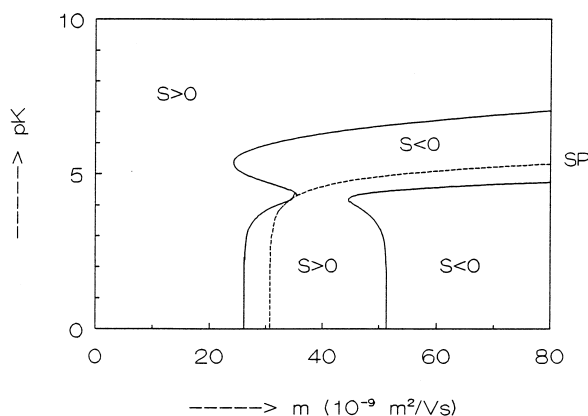


Fig. 5. Peak Shape Diagram for the same BGE as the SystChart of Fig. 4. Two contours of symmetry ($S = 0$, —) are visible and between them a discontinuity is present ($\cdot \cdot \cdot$) representing the mobility of a SP. For further information, see text.

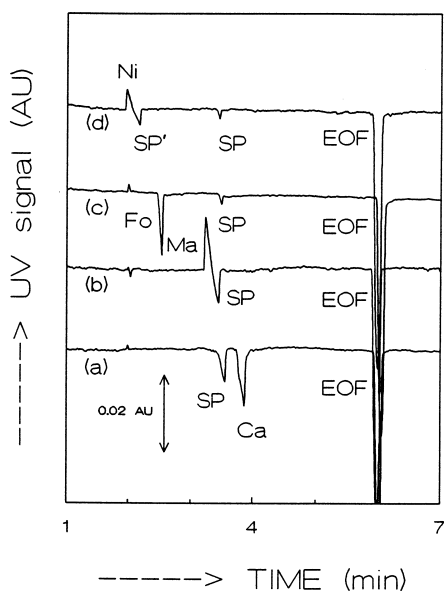


Fig. 6. Measured electropherograms for injections of 0.001 *M* solutions of (a) caproate (Ca), (b) mandelate (Ma), (c) formate (Fo) and (d) nitrate (Ni) applying a BGE of Tris phthalate at pH 5.1. CTAB was added to the BGE in order to induce anodic EOF and the anode was set at the outlet. For further information, see text.

It is strange that sometimes both the anionic sample ions and the SP are dips (Fig. 6a and c), whereas nitrate and mandelate give peaks and the SP is a dip. The SP with a mobility of ca. $-70 \cdot 10^{-9} \text{ m}^2/\text{V s}$ is caused by the addition of CTAB to the BGE and therefore bromide is a second co-ion for anionic electrolyte systems. For BGEs with two co-ions the mobility of the SP is similar to the mobility of the co-ions with the lowest concentration, here bromide. In order to avoid this SP, if needed, CTA can be added in the form of cetyltrimethylammonium hydroxide. Sample ions with mobilities near the mobilities of a SP (see Fig. 6b and d) show a large EMD and larger peak area, as observed earlier [6].

Another multivalent ionic species often used in BGEs is phosphoric acid. It is often used in BGEs for the determination of UV absorbing components, because of its lack of UV absorbance. In order to see whether SPs can be expected, the $E_1 m_1 / E_2 m_2$ relationship for anionic sample ions of the SystChart and the PSD were calculated for a BGE consisting of

0.005 *M* phosphoric acid and 0.0075 *M* sodium hydroxide at pH 7.2. The counterion sodium was used to avoid interaction in buffering capacity because of the presence of, for example, Tris with a *pK* of 8.1. Fig. 7 shows the $E_1 m_1 / E_2 m_2$ panel. The discontinuity indicates the existence of a SP. The points of symmetry are exactly at the mobilities of the monovalent and divalent phosphate ions, respectively $-35.1 \cdot 10^{-9} \text{ m}^2/\text{V s}$ and $-61.5 \cdot 10^{-9} \text{ m}^2/\text{V s}$. The calculations were carried out for strong anionic species. Fig. 8 shows the PSD for the same BGE. From Figs. 7 and 8 the same mobilities for the centers of symmetry and the SP can be obtained for strong anions. The mobility of the SP is ca. $-43.5 \cdot 10^{-9} \text{ m}^2/\text{V s}$. To verify these calculated values experimentally we carried out experiments as follows. Fig. 9 shows the measured electropherograms for injections of (a) 0.01 *M* iodate and (b) a mixture of 0.002 *M* hippurate, picrate, salicylate, phthalate and maleate. The cathode was placed at the outlet and no CTAB was added to the BGE. As EOF marker, 3 μl of mesityl oxide was added to 5 ml

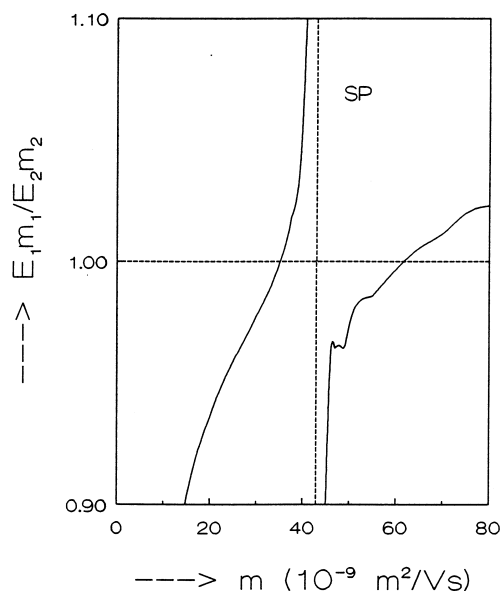


Fig. 7. Calculated relationship between $E_1 m_1 / E_2 m_2$ and mobility of sample anionic species on applying a BGE consisting of 0.005 *M* phosphoric acid and 0.0075 *M* sodium hydroxide at pH 7.2. The discontinuity at a mobility of ca. $-43.5 \cdot 10^{-9} \text{ m}^2/\text{V s}$ indicates the existence of a SP.

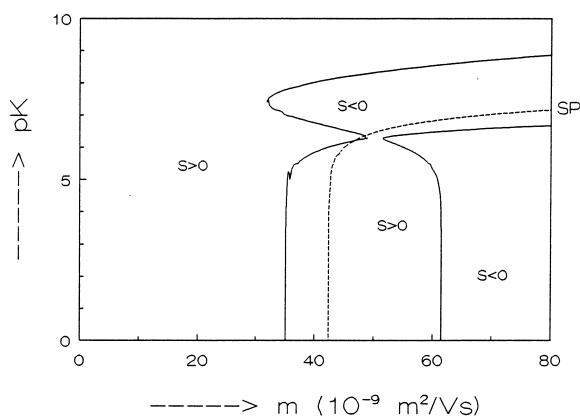


Fig. 8. Peak Shape Diagram for the same BGE at pH 7.2 as used in Fig. 7. Two contours of symmetry ($S = 0$, —) are visible and between them a discontinuity is present (· · ·) representing the mobility of a SP. For further information, see text.

sample solution. Two centers of symmetry can be observed in electropherogram (b) at the ionic mobilities of mono- and dihydrogenphosphate. The SP would have a mobility of ca. $-43.5 \cdot 10^{-9} \text{ m}^2/\text{V s}$ and therefore we carried out an experiment by injecting iodate as sample ionic species. In the first instance we injected 0.0025 M iodate and no peak

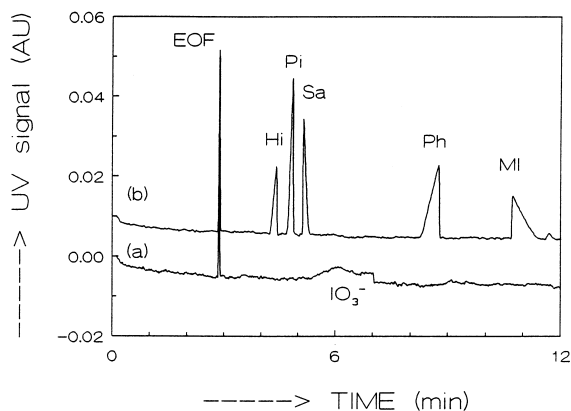


Fig. 9. Measured electropherograms for injections of (a) 0.01 M iodate (IO_3^-) and (b) a mixture of 0.002 M hippurate (Hi), picrate (Pi), salicylate (Sa), phthalate (Ph) and maleate (MI). The cathode was placed at the outlet. Three microliters of mesityl oxide was added to 5 ml of sample solution as EOF marker. Two centres of symmetry are present at the ionic mobilities of mono- and dihydrogenphosphate and an invisible SP at the position of iodate.

was obtained. Only a slight deviation in the baseline could be seen. On injecting 0.01 M iodate (see Fig. 9a) a very broad deformed peak could be observed, indicating that an invisible SP is present at the position of iodate.

3.3. Why robust BGE can fail

Section 3.2 describes and demonstrates experimentally that when applying BGEs consisting of multivalent co-ionic species, SPs can be expected in electropherograms. Nevertheless, BGEs containing multivalent ionic species are often used and considered as robust BGEs for the analysis of diverse components. Jegle [17], for example, optimized phosphate buffers with respect to pH, ionic strength, peak shape, etc., but invisible SPs were not known at that time. Also, Altria et al. [18] often applied phthalate buffers for the separation of anionic species, without investigation of the existence of SPs. In this section we will therefore consider a BGE consisting of phthalic acid and test the applicability with a view to the presence of SPs, which can be responsible for disturbances in electrophoretic separations. Altria et al. often used BGEs consisting of phthalate, 2-(*N*-morpholino)ethanesulfonic acid (MES) and tetradecyltrimethylammonium bromide (TTAB). For simplicity, we preferred to use a BGE consisting of 0.005 M phthalic acid, 0.0075 M Tris at pH 5.1 and added $5 \cdot 10^{-4} \text{ M}$ of CTAB in order to induce an anodic EOF to be able to work in anionic mode (anode placed at the outlet). In the first instance we measured a sample mixture used by Altria et al., a mixture of 0.002 M tartrate, citrate, succinate and acetate. We did it in the same way, i.e. with inversion of the detector signal, and we stopped after ca. 3.5 min (see Fig. 10a). We obtained an electropherogram which was in excellent agreement with figures given for this mixture by Altria et al. [18,19]. Because we expected that the last peak was a SP, we carried out the same experiment without inversion of the detector signal and we waited longer in order to also detect the EOF peak (see Fig. 10b). Clearly, just as in Fig. 6, we see two SPs, besides the non-moving EOF and four sample component dips. Because the EOF was a peak, and according to the adaptation of the BGE at the point of injection according to Kohlrausch's law, we diluted the mixture five times

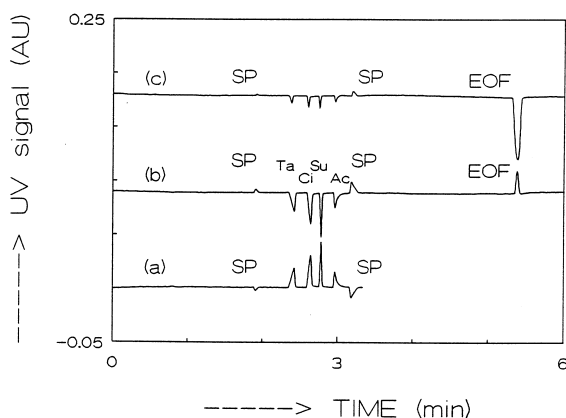


Fig. 10. Measured electropherograms for the separation of injections of (a) the "Altria" mixture of 0.002 M tartarate (Ta), citrate (Ci), succinate (Su) and acetate (Ac) with inversion of the detector signal, (b) the same mixture measured for a longer time with no inversion of the detector signal and (c) the same as (b) with five times diluted sample mixture. BGE was Tris phthalate at pH 5.1 containing $5 \cdot 10^{-4}$ M CTAB. Anode placed at the outlet. The presence of two system peaks can clearly be seen, besides the EOF dip. For further information, see text.

and re-measured the electropherogram (Fig. 10c). The EOF is now a dip. Comparing Fig. 10a–c, it can be concluded that the dips in Altria's figures are SPs. Although these SPs do not affect the separation, it is

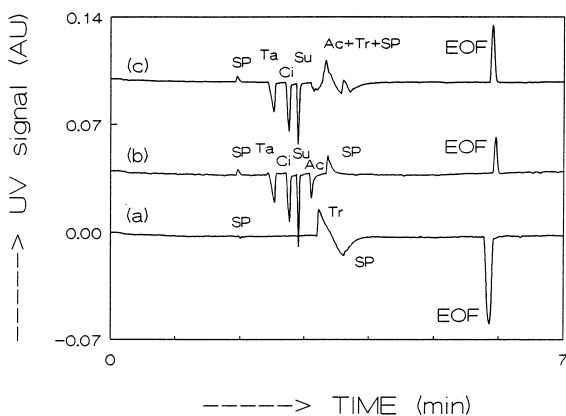


Fig. 11. Measured electropherograms for the separation of injections of (a) 0.002 M trichloroacetate (Tr), (b) a mixture of 0.002 M tartarate (Ta), citrate (Ci), succinate (Su) and acetate (Ac) and (c) a mixture of 0.002 M tartarate (Ta), citrate (Ci), succinate (Su), acetate (Ac) and trichloroacetate (Tr). BGE as in Fig. 10. For further information, see text.

obvious that application of this BGE for the separation of other anionic species can be troublesome. To show this effect, we measured a series of components applying this BGE, and for components with mobilities slower than that of acetic acid (the last of the mixture of Fig. 10b) an interaction with the SP could be observed. To demonstrate this, Fig. 11 shows electropherograms for the separation of (a) 0.002 M trichloroacetate, (b) the mixture of Fig. 10b and (c) 0.002 M of all components of Fig. 10b including trichloroacetate. In Fig. 11a it can be seen that trichloroacetate gives a huge peak, whereas the SP is a huge dip; there is a strong interaction between the component and the SP, but it is not quite clear what is the component and what is the SP. Whereas in Fig. 11b acetate is separated from the SP, in Fig. 11c the separation of acetate, trichloroacetate and the SP is completely disturbed.

4. Conclusions

SPs exist when applying BGEs with more co-ionic species, whereby hydrogen or hydroxyl ions can also act as second co-ionic species. If a SP is present, a sample zone can be affected by the presence of this SP if their mobilities are close together. If BGEs are applied containing multivalent weak components, both ionic forms of that multivalent component present at a specific pH can act as co-ions, through which a SP can originate. BGEs consisting of multivalent components are often not universally applicable and these BGEs must be handled carefully. SPs can be predicted by SystCharts or PSDs as has been demonstrated.

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