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Separation of hydrophobic polymer additives by microemulsion electrokinetic chromatography

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Abstract

Microemulsion electrokinetic chromatography (MEEKC) has been applied to the separation of some phenolic antioxidants [Irganox 1024, Irganox 1035, Irganox 1076, Irganox 1010, Irganox 1330, Irgafos 138, Irganox 168 and 2,6-di-*tert*.-butyl-4-methylphenol (BHT)]. Due to the extremely hydrophobic nature of these analytes, they could not be separated using standard MEEKC conditions and two alternative approaches were investigated. Using an acidic buffer (phosphate, pH 2.5) to effectively suppress the electroosmotic flow, the addition of 2-propanol to the aqueous phase of the microemulsion buffer to improve partitioning of the analytes, and a negative separation voltage, separation of five of the analytes in under 10 min was possible. The second approach, using a basic buffer (borate, pH 9.2) and a positive separation voltage resulted in complete resolution of all eight analytes. A mixed surfactant system comprising the anionic sodium dodecyl sulfate (SDS) and neutral Brij 35 was used to reduce the overall charge and with it the mobility of the droplets, and hence the separation time. Using an optimised MEEKC buffer consisting of 2.25% (w/w) SDS, 0.75% (w/w) Brij 35, 0.8% (w/w) *n*-octane, 6.6% (w/w) 1-butanol, 25% (w/w) 2-propanol and 64.6% (w/w) 10 m*M* borate buffer (pH 9.2) the eight target analytes were baseline separated in under 25 min. For these analytes, MEEKC was found to be superior to micellar electrokinetic chromatography in every respect. Specifically, the solubility of the analytes was better, the selectivity was more favourable, the analysis time was shorter and the separation efficiency was up to 72% higher when using the MEEKC method. Detection limits from 5.4 to 26 μg/ml were obtained and the calibration plot was linear over more than one order of magnitude. The optimised method could be applied to the determination of Irganox 1330 and Irganox 1010 in polypropylene.

Keywords: Microemulsion electrokinetic chromatography; Buffer composition; Antioxidants; Surfactants

1. Introduction

Microemulsions are dispersions of oil and water stabilised by surfactant molecules and often also an alcohol as a co-surfactant. They are made of droplets [oil in water (o/w) or water in oil (w/o) microemulsions] surrounded by a surfactant monolayer and dispersed in a continuous phase. Since 1943 these systems have been known [1] and their high solubilising power has been extensively used in industry, for example for oil recovery [2]. More recently microemulsions have been introduced to

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separation science, in particular for high-performance liquid chromatography (HPLC) [3,4] and microemulsion electrokinetic chromatography (MEEKC) [5–11].

MEEKC was first introduced by Watarai in 1991 [9] and can be classified as an extension of micellar electrokinetic chromatography (MEKC) with the micelles being replaced by oil droplets. In general, microemulsions prepared in aqueous buffer solutions (usually at an alkaline pH), with oil droplets consisting of an *n*-alkane (*n*-octane or *n*-heptane) are employed. A surfactant such as sodium dodecyl sulfate (SDS) is added to stabilise the oil droplets, together with an alcohol such as 1-butanol acting as a co-surfactant. The separation mechanism of MEEKC is similar to MEKC, but there some distinct differences and advantages of this technique.

First, in MEEKC the analytes are more readily able to penetrate the droplet than the surface of a micelle which is more rigid [10]. This means that MEEKC can be applied to solutes having a greater range of hydrophobicities than MEKC. Also, in MEKC the separation of very hydrophobic analytes is problematic as they may not be soluble in the buffer and precipitation during the separation may occur [12]. The high solubilising ability of the microemulsion allows the analysis of such solutes by MEEKC. Second, employing negatively charged microemulsion droplets and a positive separation voltage [i.e., cathodic electroosmotic flow (EOF)], MEEKC provides a separation window which is significantly larger than in MEKC. This is due to the greater mobility of the droplets in comparison to micelles. Nevertheless MEEKC also has a finite window in which neutral analytes must be eluted if they are to be separated, but in contrast to MEKC, varying the concentration of the SDS in the buffer in MEEKC allows the size of this window to be varied, as the change on the microemulsion droplets changes. Finally, MEEKC offers higher separation efficiencies than MEKC for many analytes.

Whilst MEEKC has been shown to be a method more suited to the analysis of hydrophobic analytes than MEKC due to the higher solubilising properties of microemulsion droplets over micelles, there are still some distinct disadvantages. In particular, as MEEKC is usually performed in basic conditions, the microemulsion droplets are moving against the EOF and hence move slowly towards the detector. This means that more hydrophobic analytes, which will spend a significant amount of time associated with the microemulsion droplets, will result in long separation times [6,13]. Recently, an alternative approach to MEEKC which results in faster separations of such analytes has been reported [14]. In this work, the MEEKC separation of fat soluble vitamins (vitamin A palmitate, E acetate and D_3) employing an acidic buffer (i.e., suppressed EOF) and a negative separation voltage was demonstrated. The high mobility of the microemulsion droplets meant that they, and with them the most hydrophobic analytes, migrated quickly towards the detector and short analysis times could be achieved. Additionally due to the high hydrophobicity of these analytes the use of an organic modifier (2-propanol) in the carrier electrolyte was necessary to aid separation by influencing the partition of the analytes between the droplets and the electrolyte. This method has since been extended to the analysis of several classes of pharmaceuticals (steroids, benzodiazepines, anti-depressants, anti-psychotic and anti-epileptic drugs) [15].

In the present work we investigated the feasibility of using MEEKC for the separation of some extremely hydrophobic, aromatic polymer additives (anti-oxidants) used in the production of polypropylene. The determination of these additives is important, both for reasons of health and environmental considerations [16] and also for product quality control. However, direct analysis in the polymer matrix is difficult due to the small amounts present and chromatographic analysis of extracts is therefore commonly employed. As these compounds are of relatively high molecular mass (>500 g/mol), they are usually determined by liquid chromatography (LC) [17,18] or supercritical fluid chromatography (SFC) [19,20]. Whilst the high-resolution separation of 21 additives has been reported by capillary SFC [20], in general most methods have described the separation of only two or three additives as part of a specific additive blend. Also, when using LC techniques, long analysis times (40–60 min) have to be taken into account and often complicated gradient conditions are required. Therefore the aim of this work was to investigate the potential of an electrophoretic separation method,

namely MEEKC, as a simple and relatively fast alternative for the determination of hydrophobic polymer additives in polypropylene samples. Different MEEKC approaches utilising either acidic or basic conditions and surfactant mixtures containing SDS and Brij 35 were employed. Effects caused by variation in the micromemulsion composition and the amount of an organic modifier (2-propanol) added were also investigated. The resulting MEEKC system was compared with a conventional MEKC method and the analytical potential of the developed method was evaluated with respect to the separation of some of the polymer additives in a polypropylene sample.

2. Experimental

2.1. Instrumentation

Experiments were performed using a Quanta 4000 (Waters, Bedford, MA, USA) or a HP ^{3D}CE system (Hewlett-Packard, Waldbronn, Germany). Injection was either hydrostatic by elevating the sample vial to a height of 10 cm for 10 s (Quanta 4000) or by applying a pressure of 50 mbar for 3 s (HP ^{3D}CE) as described in the figure captions. Experiments were performed either at ambient temperature (Quanta) or the capillary was thermostatted at 25°C. The analytes were detected using direct UV detection at 214 or 200 nm, respectively.

2.2. Materials and reagents

Fused-silica capillaries (50 μm I.D.×360 μm O.D.) obtained from Composite Metal Service (Hallow, UK) were used throughout this work. All capillaries were cut to total lengths of either 40 cm or 60 cm corresponding to effective lengths of 32 cm or 52 cm (Quanta 4000) or 51.5 cm (HP ^{3D}CE) as stated in the figure captions.

Water was purified using a Milli-Q (Millipore, Bedford, MA, USA) system. The polymer additives studied are shown in Fig. 1. All were obtained from Ciba-Geigy (Vienna, Austria) except 2,6-di-*tert*.-butyl-4-methylphenol (BHT) which was obtained from Merck (Darmstadt, Germany). Boric acid, orthophosphoric acid, tetrahydrofuran (spectroscopic grade), 2-propanol and 1-butanol were all obtained from Merck. SDS was obtained from Sigma (St. Louis, MO, USA), Brij 35 was obtained from Aldrich (Milwaukee, WI, USA) and *n*-octane was obtained from Fluka (Buchs, Switzerland).

All chemicals used were of analytical grade unless otherwise stated.

2.3. Preparation of microemulsions

Borate buffer was prepared from boric acid, titrated to pH 9.2 with sodium hydroxide. Phosphate buffer was prepared from orthophosphoric acid titrated to pH 2.5 with sodium hydroxide. The final microemulsion was prepared in the following way: 2.25 g of SDS, 0.75 g of Brij 35 and 6.6 g 1-butanol was mixed. Subsequently, 0.8 g *n*-octane, 25 g 2-propanol and 64.6 g of 10 m*M* borate buffer were added and the mixture was placed in an ultrasonic bath for 30 min to obtain a clear solution. The microemulsion was filtered through a 0.45-μm membrane filter before use.

2.4. Preparation of standard solutions and samples

A stock standard solution of 1–1.5 mg/ml of each analyte was prepared in tetrahydrofuran and was subsequently diluted with either the microemulsion buffer, or the micromulsion prepared with water instead of the buffer.

The samples were prepared in the following way. Approximately 0.5 g of polymer was refluxed in 30 ml of toluene for 40 min. The solution was then cooled and 40 ml of methanol was added in a dropwise fashion to precipitate the dissolved polypropylene. After filtration of the precipitate it was washed with three 10-ml portions of toluene–methanol (1:1) and the filtrate was then rotary evaporated to dryness and re-dissolved in 5 ml of acetonitrile. As this solution sometimes contained residual polypropylene, it was filtered through a 0.45-μm disk filter before use. Before analysis the sample was diluted (10:1) with the microemulsion buffer, or the microemulsion prepared with water.

Acetone was used as an EOF marker for all separations. Limits of detection (LODs) were determined at a signal-to-noise ratio of 3.

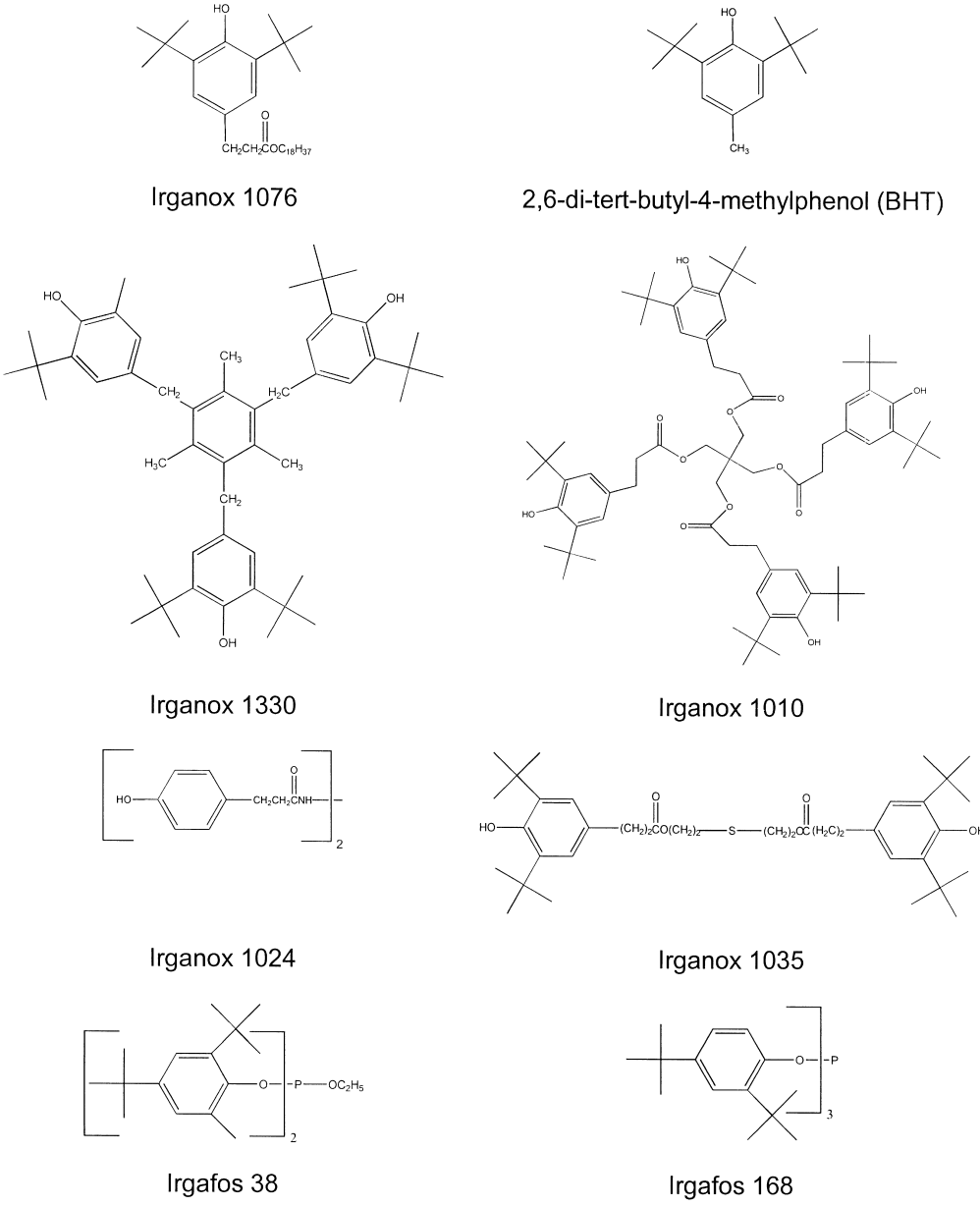

Fig. 1. Structures of the polymer additives studied in this work.

3. Results and discussion

3.1. Separation approaches

As acidic conditions (together with a negative separation voltage) had been used so successfully in the past for the separation of hydrophobic analytes [14], this approach was the first investigated. However, the extremely hydrophobic nature of these particular analytes meant that aside from the separation conditions, there were problems encountered when dissolving the standards. Specifically, some of the selected analytes (e.g., Irganox compounds, BHT) were soluble at low concentrations in acetoni-

trile, whereas others such as Irgafos 168 and Irgafos 38 were only soluble in tetrahydrofuran, or a mixture of the two solvents. Therefore tetrahydrofuran was used as the solvent for all analytes. As a consequence, the standards had to be diluted in the microemulsion buffer before injection, so as to avoid the introduction of a solvent plug that would destroy the microemulsion [5].

Taking as a starting point a MEEKC system published for the separations of hydrophobic analytes [14] at low pH, several modifications were made to ensure its compatibility with the analytical problems investigated in this study. First, the microemulsion described in the literature used up to 6% SDS; but this was found to produce unacceptably high currents and the amount of surfactant was reduced to 3% in this work. Second, when employing a purely aqueous system, only a single peak was obtained suggesting that all the analytes were entirely included in the microemulsion phase. Therefore, 20% 2-propanol was added to the microemulsion buffer in order to promote partitioning into the aqueous phase. This approach was initially successful, resulting in the separation of five of the seven selected analytes as shown in Fig. 2, but when the amount of 2-propanol in the buffer was increased to more than 20% to further influence the partitioning coefficient, the system became unstable and an erratic current was obtained. Similar problems were obtained with other solvents such as acetonitrile, tetrahydrofuran or 1-butanol. This led to the conclusion that this system was not suitable for the separation of all the selected analytes and therefore further work was performed using a basic carrier electrolyte providing a substantial cathodic EOF in combination with a positive separation voltage.

The microemulsion subsequently used was initially based on the first MEEKC system described by Watarai [9] which has formed the basis of most works published so far. For this reason microemulsions with the following compositions were investigated: 3% (w/w) surfactant (SDS or SDS/Brij 35 as discussed in detail in Section 3.2.2), 6.6% (w/w) 1-butanol, 0.8% (w/w) *n*-octane, 0–25% (w/w) 2-propanol and 64.6–89.6% (w/w) 10 m*M* borate buffer. The optimisation of this system for the separation of the selected analytes is described in detail in the following section.

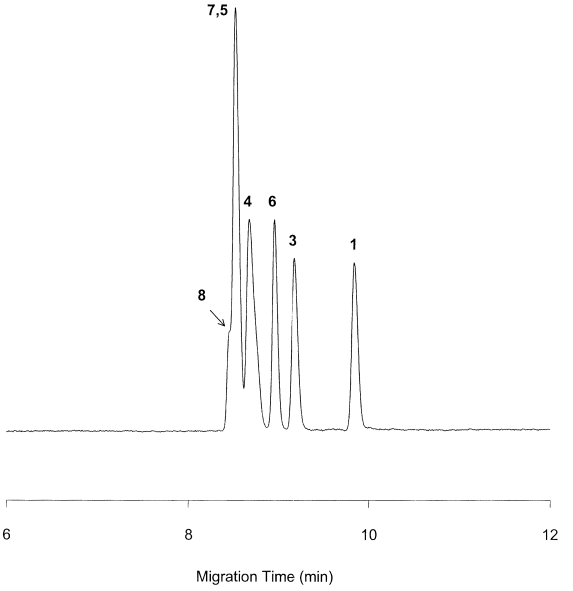

Fig. 2. Separation of seven polymer additives in an acidic microemulsion buffer (suppressed EOF conditions). Capillary: 40 cm (32 cm to detector)×50 μm I.D. Microemulsion buffer: 3% (w/w) SDS, 6.6% (w/w) 1-butanol, 0.8% *n*-octane, 20% (w/w) 2-propanol, 69.6% (w/w) 25 m*M* phosphate buffer (pH 2.5). Injection: hydrodynamic, 10 cm for 10 s. Voltage: −20 kV. Temperature: 26°C. Detection: direct UV, 214 nm. Standard prepared in water. Peaks: 1=Irganox 1024, 2=BHT, 3=Irganox 1035, 4=Irgafos 38, 5=Irgafos 168, 6=Irganox 1010, 7=Irganox 1330, 8=Irganox 1076.

3.2. Optimisation of the microemulsion buffer

3.2.1. Addition of organic modifier

In a manner similar to the results obtained using acidic separation conditions, there was effectively no separation of the analytes when a purely aqueous buffer was employed (Fig. 3a). Therefore, 2-propanol was added to the separation buffer to facilitate partitioning of the solutes from the oil droplets into the bulk electrolyte. This led to a baseline separation of all the analytes when the concentration of 2-propanol in the buffer was increased from 0 to 25%, as can be seen from Fig. 3. Concentrations above 25% 2-propanol could not be used as the system became unstable with regard to the baseline and current obtained. Other solvents, including acetonitrile, methanol or ethanol were also investigated but concentrations above 10% led to an increased destabilisation of the system, in particular with regard

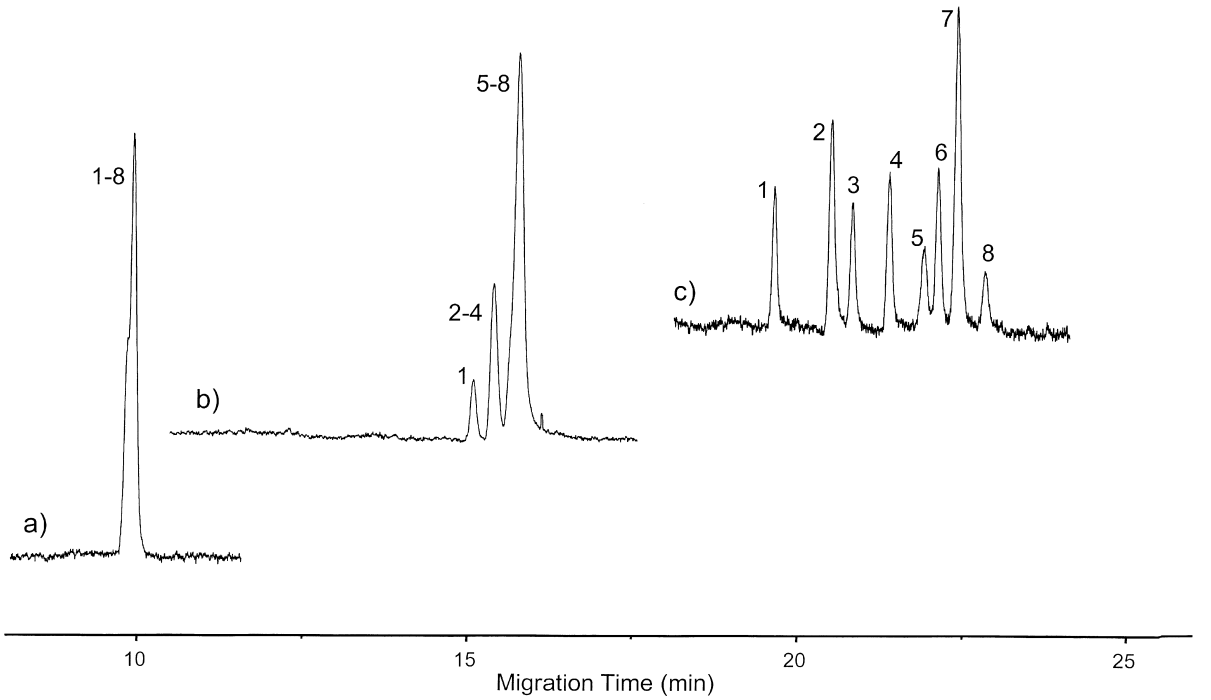

Fig. 3. Effect of varying the amount of 2-propanol in the microemulsion buffer. Capillary: 60 cm (52 cm to detector)×50 μm I.D. Microemulsion buffer: 2.25% SDS (w/w), 0.75% Brij 35 (w/w), 6.6% 1-butanol (w/w), 0.8% *n*-octane and (a) 0% (w/w) 2-propanol, 89.6% (w/w) borate buffer (pH 9.2), (b) 10% (w/w) 2-propanol, 79.6% (w/w) borate buffer (pH 9.2), (c) 25% (w/w) 2-propanol, 64.6% (w/w) borate buffer (pH 9.2). Voltage: +30 kV. Temperature: 24°C. All other conditions as given in Fig. 2.

to the microemulsion. It is proposed that this did not occur with 2-propanol because it acts as a co-surfactant and therefore may be used in higher amounts without destruction of the microemulsion droplets [10]. An additional benefit of 2-propanol was that it also reduced the current and further increased the solubilising capacity of the buffer. As the linear range of this technique is limited by the solubility of the analytes in the carrier electrolyte, the latter fact is of particular importance when considering the applicability of this method for the analysis of real samples.

3.2.2. Surfactant composition

When using the MEEKC system with 3.3% (w/w) SDS (similar to that most commonly reported in the literature), extremely long separation times were obtained. This fact can be explained by the high surface charge of the microemulsion droplets which means that they moved very slowly towards the detector and none of the analytes could be detected within 60 min. Therefore, a mixed surfactant system comprising SDS and the neutral surfactant Brij 35 was employed. In this case, the benefits of a mixed surfactant system were threefold. First, in the mixed surfactant system the overall charge of the microemulsion droplets and with it their electrophoretic mobility (towards the anode) was greatly reduced resulting in much faster separations. Second, by replacing some of the SDS with a neutral surfactant the separation current was significantly lowered. Third, the use of the mixed surfactant system also resulted in changes in separation selectivity. Specifically, selectivity changes for Irganox 1010, Irgafos 168 and Irgafos 38 can be seen when comparing Figs. 2 and 3c). Although these two separations are at different pH (pH 2.5 and pH 9.2, respectively) it is reasonable to assume that the changes in separation selectivity are due to the change in surfactant composition, as the ionisation of these analytes should not change over this pH range.

Mixed surfactant systems have been described

previously, particularly when investigating the separation selectivity in MEEKC [21]. However, to our knowledge no work has been published concerning the optimisation of the exact surfactant composition in such a system. Also the effects on the separation caused by variations in the ratio of the different surfactants have not been investigated up to now. In this work, the composition of the ratio of the two surfactants was optimised with respect to the separation selectivity and separation time and the results are illustrated in Fig. 4. Regarding this figure, the fastest separation was obtained with a surfactant ratio of SDS–Brij 35 (1:1) (Fig. 4a) where the charge on the droplet was lowest. Nevertheless this composition did not result in complete resolution of the analytes. As the fraction of Brij 35 was decreased, the separation selectivity changed to allow complete separation of the analytes at a ratio SDS–Brij 35 (4:1) (Fig. 4d). Although a further reduction of the Brij 35 concentration resulted in improved resolution, it also led to longer separation times. The separation selectivity was not only influenced by the surfactant ratio but also by the amount of 2-propanol added to the running buffer. For this reason manipulating these two parameters could be used to optimise the separation time. This can be seen by comparing the separations depicted in Fig. 4d (20% 2-propanol, surfactant ratio of 4:1) and Fig. 3c (25% 2-propanol, surfactant ratio of 3:1). In both cases similar selectivities were obtained but the latter composition led to a significantly faster separation and therefore was chosen as the final separation system.

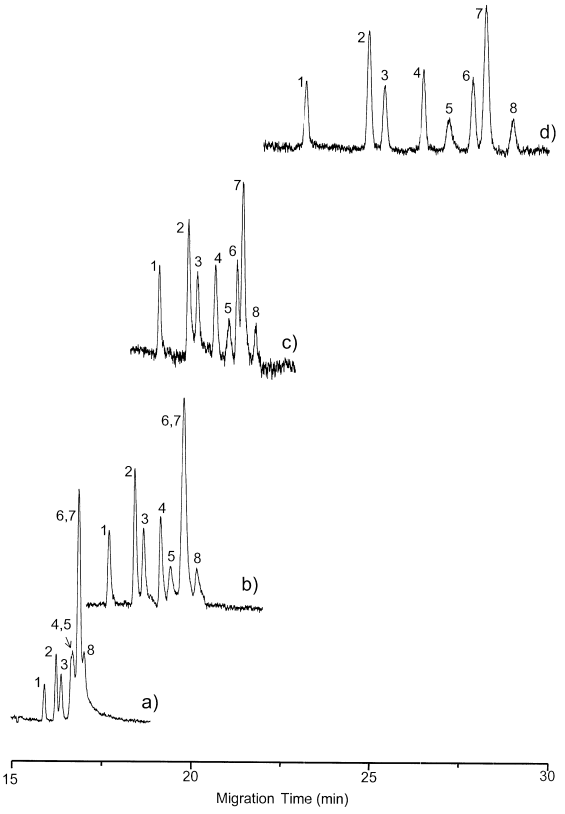

Fig. 4. Effect of varying the surfactant ratio in the microemulsion buffer. Microemulsion buffer: 6.6% (w/w) 1-butanol, 0.8% (w/w) *n*-octane, 20% (w/w) 2-propanol, 69.6% (w/w) borate buffer (pH 9.2) and (a) (1:1) 1.5% (w/w) SDS, 1.5% (w/w) Brij 35, (b) (2:1) 2% (w/w) SDS, 1% (w/w) Brij 35, (c) (3:1) 2.25% (w/w) SDS, 0.75% (w/w) Brij 35, (d) (4:1) 2.4% (w/w) SDS, 0.6% (w/w) Brij 35. Temperature: 25°C. All other conditions as given in Fig. 2.

3.3. Comparison with MEKC

Whilst it has been shown previously that MEEKC has several advantages over MEKC, there have been few direct comparisons, especially for the separation of strongly hydrophobic analytes as used in this work. Furthermore, we are not aware of any examples in the literature providing a comparison of MEEKC and MEKC systems containing such a high amount of organic modifier that may cause significant changes in the structure of the micelles/microemulsion droplets compared to predominantly aqueous systems. Therefore a critical investigation of the two techniques may be useful to elucidate more about the exact separation mechanisms involved.

Three different separation buffers were considered in order to facilitate a comparison of MEEKC and MEKC. These included: (a) the optimised MEEKC buffer [2.25% (w/w) SDS, 0.75% (w/w) Brij 35, 0.8% (w/w) *n*-octane, 6.6% (w/w) 1-butanol, 25%% (w/w) 2-propanol and 64.6% (w/w) 10 m*M* borate buffer (pH 9.2)]. (b) The optimised MEEKC buffer without *n*-octane. (c) The optimised MEEKC without *n*-octane and 1-butanol.

This procedure was chosen based on the following reasoning. First, in order to investigate the system without the microemulsion droplets present the *n*-octane is omitted from the buffer. As there should be

both microemulsion droplets and micelles present in the microemulsion system, then only the micelles should remain under these conditions. However, it is also incorrect to assume that this system contains simply micelles. In particular, it is known that 1-butanol (at approximately the concentration used in this work) will penetrate into the structure of SDS micelles, reducing the charge density, forming more dissociated micelles and reducing the critical micellar concentration (CMC) substantially [22]. In this way the system should therefore contain ''modified micelles'' which in may behave in a similar way to the microemulsion droplets, with the 1-butanol replacing the oil phase. Second, in order to compare both a and b with a system that is purely micellar, both the oil (*n*-octane) and co-surfactant (1-butanol) were omitted. In summary, this regime allows a comparison of MEEKC, the MEEKC system without the microemulsion droplets, and a purely micellar system and the results of this comparison are depicted in Fig. 5. From this figure several things are apparent. The separations obtained in a and b were quite similar, suggesting that the analytes partition into the ''modified micelles'' in a similar way as they do into the microemulsion droplets. This demonstrates that a modified micellar phase alone is effective for the separation of such hydrophobic analytes. There is a significant selectivity difference between both a and b and c, which means that the purely micellar phase differs significantly from either the microemulsion or the modified micellar phases. Unfortunately, the MEKC system resulted in solubility problems for these analytes, as the standard did not dissolve in the buffer. Consequently it was necessary to dissolve it in a mixture of 2-propanol–MEKC buffer (1:1). These problems with solubility would invariably lead to precipitation problems during the separation process if a higher concentration of the analytes was injected.

In evaluating the best separation system, it is clear that MEEKC was superior in several respects. Better separation was achieved with the inclusion of the microemulsion droplets, and the separation was faster. Also MEEKC offered an improvement in separation efficiency of 5–48% over the system without 1-butanol and 30–72% over a purely micellar system. Finally the MEEKC system showed a better ability to solubilise the analytes, thus offering

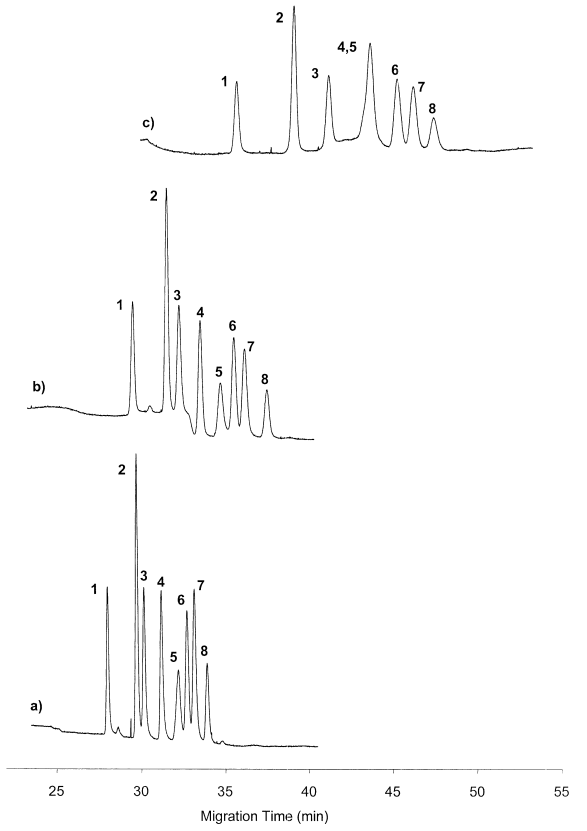

Fig. 5. Comparison of MEEKC and MEKC separations. Capillary: 60 cm (51.5 cm to detector)×50 μm I.D. Microemulsion buffer: 2.25% (w/w) SDS, 0.75% (w/w) Brij 35, 6.6% (w/w) 1-butanol, 0.8% (w/w) *n*-octane, 25% (w/w) 2-propanol, 64.6% (w/w) borate buffer (pH 9.2). Standard prepared in buffer. Separations are using (a) microemulsion buffer, (b) microemulsion buffer without *n*-octane, (c) microemulsion buffer without *n*-octane and 1-butanol. Injection: pressure, 50 mbar, 3 s. Temperature: 25°C. Detection: direct UV, 200 nm. All other conditions as in Fig. 2.

greater analytical potential. Therefore MEEKC can be regarded as the best alternative for the separation of the selected analytes.

3.4. Analytical performance

The analytical performance of the chosen MEEKC system was investigated with respect to the linear range, detection limits and separation efficiencies for each analyte and the results are depicted in Table 1. Reproducibilities of migration times and peak areas, as determined by 10 consecutive injections, were less

Table 1
Comparison of the linear range, detection limits and separation efficiencies for all the analytes studied

	Linear range (μg/ml)	Detection limit (μg/ml)	Efficiency (plates/m)
Irganox 1024	23–792	13	391 000
BHT	54–807	20	408 000
Irganox 1035	33–794	20	344 000
Irgafos 38	22–829	5.4	354 000
Irgafos 168	21–1198	16	140 000
Irganox 1010	22–820	13	261 000
Irganox 1330	24–419	14	262 000
Irganox 1076	29–1195	26	298 000

All conditions as given in Fig. 5a.

than 1% relative standard deviation (RSD) for migration times and 6% RSD for peak areas for all analytes. This uncertainty can be regarded as acceptable for a MEEKC method, and in this case is acceptable for the application of the method to the determination of these additives in polypropylene. The linear range was determined using corrected peak areas (peak area/migration time) with $r^2 >$ 0.9978 for every analyte. In each case the linear range extended over one order of magnitude and was limited by the insolubility of the analytes at higher concentrations. Detection limits ranged from 5.4 to 26 μg/ml which is satisfactory for an electrophoretic separation technique using UV detection and is more than adequate for the determination of these analytes in the selected polypropylene samples. If necessary, the detection limits could be further reduced by the use of a capillary with a bubble cell. The separation efficiencies achieved were excellent, ranging from 140 000 to 408 000 plates/m as indicated in Table 1.

Additionally, the potential of this method for the analysis of a real sample could be demonstrated by the determination of Irganox 1330 and Irganox 1010 in polypropylene samples as shown in Fig. 6. Both samples shown in this figure contained Irgafos 168 together with Irganox 1010 (a) or Irganox 1330 (b), respectively, however this could not be detected as was completely oxidised by the sample preparation method used and the oxidation product, though UV absorbing could not be detected at this concentration. Therefore alternative sample preparation methods are now being investigated that do not result in the oxidation of this analyte. Additionally, although only one of the analytes was determined in each of the samples, it demonstrates that this method can potentially be applied without modification to the determination of any of the analytes in polypropylene samples.

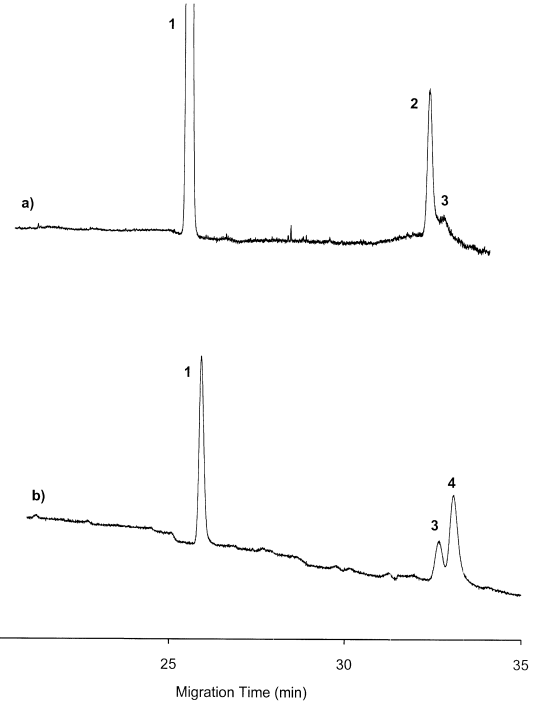

Fig. 6. Determination of polymer additives in a polypropylene samples using the optimised MEEKC conditions. Microemulsion buffer: 2.25% (w/w) SDS, 0.75% (w/w) Brij 35, 6.6% (w/w) 1-butanol, 0.8% (w/w) *n*-octane, 25% (w/w) 2-propanol, 64.6% (w/w) borate buffer (pH 9.2). Peaks: 1=toluene, 2=Irganox 1010, 3=unknown, 4=Irganox 1330. All other conditions as in Fig. 5.

4. Conclusions

MEEKC has been successfully applied to the separation of some extremely hydrophobic polymer additives. Although it was not possible to separate these analytes using a conventional MEEKC system, two different approaches were investigated for their separation. When an acidic buffer and a negative separation voltage were used, incomplete separation of the analytes resulted. However by using an alkaline buffer together with a positive separation voltage, baseline separation of all eight analytes was achieved in under 25 min. In contrast to most

previous MEEKC systems, a mixed surfactant phase comprising SDS–Brij 35 (3:1) was utilised, with the neutral Brij 35 being used to reduce the mobility of the microemulsion droplets, thereby allowing faster separations to be achieved. It was also necessary to add a substantial amount (25%, w/w) of 2-propanol to the buffer so that the analytes would partition out of the microemulsion droplets. Detailed comparison with MEKC demonstrated that MEEKC is a superior separation method for these analytes, with respect to the separation time, selectivity and efficiency.

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