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Comparison of separation selectivity in capillary electrokinetic chromatography using a cationic linear polymeric pseudo-stationary phase or monomeric additives of similar structure

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Abstract

The retention properties in electrically driven systems with monomeric additives were compared to an electrokinetic chromatographic system with a linear, charged polymer of similar chemical structure (all additives are quaternary tetraalkyl ammonium ions). The monomeric additives were tetramethylammonium (TMA), tetraethylammonium (TEA) and dimethylpyrrolidinium (DMP), respectively, the polymeric additive was poly(diallyldimethyl)ammonium (PDADMA). The additive concentration in the background electrolyte was 2 and 4% (w/w). The retention characteristics were based on the apparent mobilities of 10 non-charged analytes with different chemical functionality, which were transported by the anodic electroosmotic flow in the dynamically coated capillary, and retained by the counter-flowing cationic additives. From these data capacity factors were derived, which ranged up to 0.8. Association constants were calculated, and were found between 10 and 170. Roughly, the association constants increased for a given analyte in the sequence TMA<TEA<DMP< PDADMA. However, changes in the retention order were observed for some cases, reflecting the different selectivity of the particular systems for certain pairs of analytes. A general advantage of polymeric pseudo-stationary phases compared to monomeric additives is given by the negligible reduction of the mobility of the analyte–polymer associate in relation to the free additive ion, resulting in a broader retention window under most practical conditions.

Keywords: Selectivity; Electrokinetic chromatography; Pseudo-stationary phases; Background electrolyte composition; Electrochromatography

1. Introduction

Polymers, added as pseudo-stationary phases in electrokinetic chromatography, can serve as an alternative to micelles in micellar electrokinetic chromatography (MEKC). They have a number of advantages, e.g., they are not limited to a certain concentration, the critical micellar concentration (CMC). Up to now, several types of soluble pseudo-stationary phases have been employed, like e.g., acrylate copolymers [1–8] and polyallylamine-supported phases [9–11]. Due to their covalently fixed structure certain polymers, named ''micelle'' polymers [12–25], exhibit a higher stability in aqueous–organic media than conventional micelles. Dendrimers [26–34], calixarenes [35–37] and resorcarenes [38–40]

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supplemented the great variety of macromolecular separation additives.

In previous work we have already reported the application of cationic polymers as pseudo-stationary phase [41–44]. With polyethyleneimine as additive separation of neutral analytes was demonstrated [41,45], and the influence of organic solvents on the separation was investigated [42]. With a pseudo-stationary phase consisting of poly-(diallyldimethyl)ammonium (PDADMA), it was possible to determine capacity factors and characterise the separation system by solvation parameters [44]. Recently, we reported the relation between diffusion coefficients and capacity factors in this system [43].

It is, however, questionable if in fact a polymer structure is a prerequisite for separation of neutral analytes in electrokinetic systems. For ionic separands both cationic polymers [46–51] and cationic monomers [52,53], were employed as additives in order to change selectivity in capillary electrophoresis (ion-exchange electrokinetic chromatography). Concerning monomeric additives for separation of neutral compounds, tetraalkylammonium ions are well established in MEKC. For instance, cetyltrimethylammonium bromide is a very common surfactant [54,55]. In MEKC such quaternary ammonium salts are often used to widen the elution window [56–58].

An early application of Walbroehl and Jorgenson [59] demonstrated the separation of neutral analytes with non-micellar tetraalkylammonium salts, attributed to so-called solvophobic interaction. Subsequently, different quaternary ammonium ions were applied as pseudo-stationary phase for the separation of neutral compounds [60–64]. For example, with tetradecylammonium ions (below the CMC) separation of fat-soluble vitamins was achieved in acetonitrile–water media [62,63]. Anionic monomeric additives like sodium dioctylsulfosuccinate [65] and sulfonated Brij-30 (Brij-S) [66,67] were also introduced as pseudo-stationary phases for electrokinetic chromatography.

It is the goal of the present paper to compare the retention of the electrokinetic chromatographic system with either a polymeric additive or monomeric additives of a similar functionality, both applied as a pseudo-stationary phase. The polymeric additive – PDADMA – is a linear and soluble polyelectrolyte with quaternary ammonium with a five-ring system (Fig. 1), which served as separation medium in previous papers. The monomeric additives were tetramethylammonium (TMA), tetraethylammonium (TEA) and *N*,*N*-dimethylpyrrolidinium (DMP) ions, respectively. The comparison of the separation selectivity was based on the relative retention time, the mobility, the capacity factors, and finally the association constants. The question whether polymers possess a principle advantage compared to monomeric additives (with the same chemical interaction with the analytes) or not was examined. The discussion is based on the parameters decisive for the retention window in these separation systems.

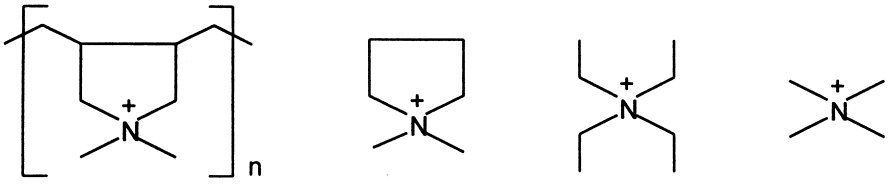

Fig. 1. Chemical structures of the additives containing quaternary ammonium functionality; PDADMA: poly(diallyldimethylammonium); DMP: *N*,*N*-dimethylpyrrolidinium; TEA: tetraethylammonium; TMA: tetramethylammonium.

2. Experimental

2.1. Chemicals

Poly(diallyldimethyl)ammonium chloride of average molecular mass 200 000–350 000 (20%, w/w, solution in water), tetramethylammonium chloride (97%) and tetraethylammonium chloride (95%) were obtained from Aldrich (Vienna, Austria). *N*,*N*-Dimethylpyrrolidinium chloride was synthesised as described below. Sodium acetate trihydrate, glacial acetic acid and ethanol (all analytical grade) were purchased from E. Merck (Darmstadt, Germany). Methyl iodide (purum), silver chloride and 1-methylpyrrolidine (analytical grade) were obtained from Fluka (Buchs, Switzerland). Analytes (E. Merck or Fluka) were used in analytical grade, except 1,3-dinitrobenzene and benzophenone (purum) and 1-naphthaldehyde (pract.). Reagents and standard solutions were prepared in double distilled water. Samples had concentrations of 1 to 5 m*M* (depending on the running buffer to get comparable UV signals).

2.2. Apparatus

The electrokinetic measurements were performed on two different capillary electrophoretic systems. The P/ACE 2100 electrophoresis system (Beckman, Fullerton, CA, USA) was equipped with an on-column UV absorbance detector (214 nm). The ^{3D}CE instrument (Hewlett-Packard, Waldbronn, Germany) was operated with a diode array detector at 214 nm. Fused-silica capillaries (Composite Metal Services, Hallow, UK) with effective and total lengths of 20.0 cm and 27.0 cm (P/ACE instrument) and 23.6 cm and 32.1 cm (^{3D}CE system) were used. New capillaries (50 μm I.D.×375 μm O.D.) were dynamically coated with PDADMA; the explicit coating procedure was carried out only at the beginning of a series of measurements, but not between the runs.

Samples were injected by pressure (35 mbar) for 1 s to 5 s. In the case of polymer-containing buffers of high viscosity an additional plug of background electrolyte (BGE) (5 s, 35 mbar) was injected after the sample. Applying a constant voltage of −3.0 kV or −4.0 kV, respectively, the resulting current was between −25 μA and −81 μA. All measurements were carried out at a 25.0°C thermostating temperature.

2.3. Procedures

2.3.1. Capillary treatment and BGE additive

The capillary was treated with a solution of 4% (w/w) PDADMA in water, which provided a dynamic, positively charged coating. The mobility of the (anodal) electroosmotic flow (EOF) occurring after this coating procedure was determined from the negative water peak. The running buffers were prepared with the additive (PDADMA chloride, DMP chloride, TEA chloride, TMA chloride) and 20 m*M* sodium acetate. Acetic acid was added to adjust the pH to 5.2. All additives had a concentration of 2% (w/w) or 4% (w/w), respectively.

2.3.2. Determination of the mobilities of the additives

The mobilities of the cationic monomers at 10 m*M* and those of chloride (the counter-ion) at various concentrations were taken from the literature [68,69]. The mobilities TMA and TEA were obtained based on these literature data indirectly by measuring the current in the capillary at concentrations of 10 m*M*, 2% (w/w) and 4% (w/w). For DMP an absolute value was not calculated, but the relative change of the additive mobility for 2% and 4% (w/w) (needed for the calculation of K_i) was supposed to be the same as for TMA. The mobility of PDADMA at 4% (w/w) was determined in a previous work [44].

2.3.3. Synthesis of N,N-dimethylpyrrolidinium chloride

DMP iodide was prepared by reaction of *N*-methylpyrrolidine with methyl iodide in absolute ethanol [70]. After stirring an aqueous solution of the iodide salt with silver chloride the silver salts were filtered off and the solvent was removed under reduced pressure. DMP chloride was crystallised from ethanol–acetone (25:75). The structure of the molecule was proved by ^{1}H nuclear magnetic resonance (NMR) and its composition by elemental analysis.

3. Results and discussion

A measure for the extent of retardation of an analyte, *i*, in a chromatographic system, is the capacity factor, k_i. It reflects the interaction between analyte and stationary or pseudo-stationary phase, respectively. It is directly connected to the thermodynamic constant, K_i, the distribution constant by:

$$k_i = K_i q \quad (1)$$

where q is the phase ratio, the volume ratio of stationary and the mobile phase.

For systems with a pseudo-stationary phase like micelles or soluble polymeric additives, an analogue description can be used. Here the mobile phase is the ''free'' solvent. To be able to compare selectivity in systems with monomeric and polymeric additives, respectively, we can even extend the analogy, and describe the retention of an analyte when driven with the EOF in the mobile phase, the free solution, through the separation capillary, and retained by association with the additives. It is clear that a distinction between mobile and stationary phase might be plausible for the case of a polymer, for a monomeric additive it is hardly adequate. However, the association constant describes the extent of interaction of the analyte between the additive, on the one hand, and the solvent, on the other hand. The association constant, K_i, is given here as the ratio of the mole fractions, x_i, of analyte, *i*, associated with the additive, or free in solution (and not the concentration ratio as usual):

$$K_i = \frac{x_i^{\text{add}}}{x_i^{\text{solv}}} \quad (2)$$

The term association constant is used here instead of distribution constant, because the latter is rather related to a partitioning between two phases. However, for separation systems consisting of monomeric additives the capacity factor can be used formally in the same way as defined in Eq. (1).

3.1. Capacity factor and mobility

In all systems the retention times of the analytes were determined at 2% and 4% (w/w) additive concentration, each. All measurements were carried out in duplicate, with the simultaneous determination of the EOF. The retention times, related to the EOF, were reproducible within less than 1%, expressed by the span (only in the 4% DMP system the span was about 5%). It is obvious that for more quantitative comparison of the separation selectivity other measures than the retention time are more appropriate: the mobility, the capacity factor, and, most fundamentally, the association constant.

It should be pointed out that different mobilities must be distinguished in separation systems like the present ones. Apparent mobilities (with the superscript app in the following text) are those measured with the spatial coordinates of the capillary as the reference system. In contrast, the real or electrophoretic mobilities (with the superscript 0) are related as is common in physical chemistry to the single ion. These mobilities are not connected to the capillary as reference.

Therefore the following mobilities are distinguished (beside the mobility of the EOF, μ_{eof}): $\mu_{\text{i}}^{\text{app}}$, the apparent mobility of the *i*th analyte, measured in the usual way from the migration time and the migration distance; $\mu_{(i+\text{add})}^{\text{app}}$, the apparent mobility of the analyte–additive associate; $\mu_{\text{add}}^{\text{app}}$, the apparent mobility of the additive; $\mu_{(i+\text{add})}^{0}$, the real mobility of the analyte–additive associate; μ_{add}^{0}, the real mobility of the additive.

In the equations describing the analyte migration the mobilities must be treated as signed quantities. For convention, mobilities of positively charged particles have positive, negatively charged ones have negative sign. The real mobilities, although related to the conductivity, are signed, too, as soon as the particle transport is considered. The EOF mobility has positive sign when flowing towards the cathode, and negative (as in the present case) when directed towards the anode.

The apparent mobility, μ_i^{app}, of the *i*th analyte is:

$$\mu_i^{\text{app}} = \frac{1}{1+k_i} \cdot \mu_{\text{eof}} + \frac{k_i}{1+k_i} \cdot \mu_{(i+\text{add})}^{\text{app}} \quad (3)$$

With the capillary as the reference system the apparent mobility of the associate is the vectorial sum of the real mobility, $\mu_{(i+\text{add})}^{0}$, of the associate and the mobility of the EOF:

$$\mu_{(i+\text{add})}^{\text{app}} = \mu_{(i+\text{add})}^{0} + \mu_{\text{eof}} \quad (4)$$

The apparent mobilities, μ_i^{app}, determined experimentally in different separation systems containing 4% (w/w) additive each, are given in Table 1. They are in the range between 9 and $26 \cdot 10^{-9}$ m^2 s^{-1} V^{-1}. As the EOF varies (especially in the DMP systems), the mobilities were corrected by that of the EOF, determined in the same run. These differences, $|\mu_i^{app} - \mu_{eof}|$, are shown in Fig. 2. They depend on the real mobility of the additive–analyte complex, and on the capacity factor, which follows from Eqs. (3) and (4):

$$\mu_i^{app} - \mu_{eof} = \frac{k_i}{1 + k_i} \cdot \mu_{(i+add)}^0 \quad (5)$$

The analytes are sorted in Fig. 2 in the sequence of increasing differences in the PDADMA system that is considered as a reference. It can be seen that in the monomeric systems this sequence is not followed, seemingly reflecting selective changes in the migration behaviour of the analytes in the particular systems.

The capacity factor, k_i, derived from Eqs. (3) and (4) is:

$$k_i = \frac{\mu_{eof} - \mu_i^{app}}{\mu_i^{app} - \mu_{eof} - \mu_{(i+add)}^0} \quad (6)$$

Consequently the association constant, K_i, as defined in Eq. (1) is:

$$K_i = k_i / q = \frac{n^{solv}}{n^{add}} \cdot \frac{\mu_{eof} - \mu_i^{app}}{\mu_i^{app} - \mu_{eof} - \mu_{(i+add)}^0} \quad (7)$$

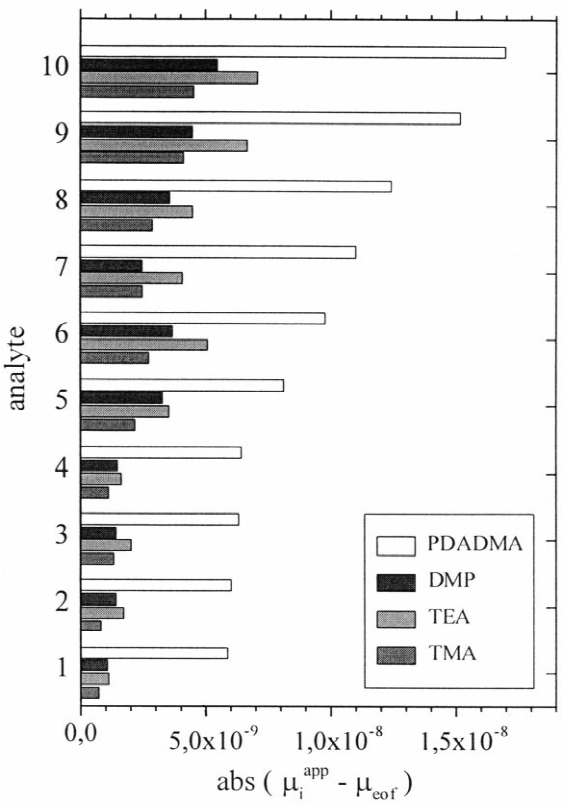

Fig. 2. Apparent mobilities of the analytes corrected by the mobility of the EOF determined in the same run. The data are shown for the four systems with the polymeric additive PDADMA and the monomeric additives TMA, TEA and DMP (concentration 4%, w/w). Numbering of the analytes as in Table 1.

Table 1
Apparent mobilities, μ_i^{app}, of the analytes in 4% (w/w) solutions of the additives[a]

No.	Analyte	μ_i^{app} ($\cdot 10^{-9}$ m^2 s^{-1} V^{-1})			
		PDADMA	TMA	TEA	DMP
1	1,3-Dinitrobenzene	26.2	21.2	22.8	15.7
2	1,4-Naphthoquinone	26.1	20.9	22.1	10.7
3	Benzyl alcohol	25.8	20.4	21.8	12.3
4	2-Nitrobenzaldehyde	25.6	20.4	22.1	8.6
5	Benzophenone	24.0	19.3	20.9	12.4
6	1-Naphthaldehyde	22.3	18.9	18.8	10.0
7	Hydroquinone	21.1	19.4	19.8	9.0
8	Resorcinol	19.6	18.7	19.4	11.6
9	2-Naphthol	16.9	17.6	16.5	11.5
10	1-Naphthol	15.7	17.2	16.3	13.6

[a] Measuring error see text.

where n^{solv} and n^{add} are the mole numbers of additive and solvent, respectively.

Eq. (7) allows one to calculate the capacity factors from the measured difference between the apparent mobility and that of the EOF, given that the real mobility of the analyte–polymer associate, $\mu^0_{(i+add)}$, is known. For the polymeric additive the situation is clear, as it can be assumed that the real mobility of the associate is nearly the same than that of the polymer. This assumption allows one to replace $\mu^0_{(i+add)}$ in the equations by μ^0_{add}. The polymer mobility can be obtained from independent measurements, and the capacity factors can be calculated thus easily for the polymeric systems.

On the other hand, the capacity factors cannot be derived such simply according to Eq. (7) for the systems containing the monomeric additives, because $\mu^0_{(i+add)}$ can hardly be measured directly. As the size of the monomeric additive is in the same order than that of the analyte, the mobility of the associate will be smaller and can differ significantly from that of the monomeric additive. Nevertheless, the association constants (and consequently the capacity factors) can be derived indirectly from the measurement of the mobility at two different additive concentrations, say, for 2 and 4% (w/w) additive concentration. We can suppose that the real mobility $\mu^0_{(i+add)}$ of the analyte–additive associate depends on the additive concentration to a minor extent (those of the monomeric additives changes by only 5 to 10%). It is evident from physico–chemical meanings that the effect on the association constant, K_i, is even smaller. Then Eq. (6) can be used for the determination of the capacity factors, as the other quantities are experimentally easily available for both concentrations of the additive.

The capacity factors, as obtained in the above described ways, are given in Table 2. It is seen that they are considerably low. Even in the system with the polymeric additive values higher than 0.8 are not exceeded. This is in contrast to micellar systems, where large capacity factors can result. Unfortunately, the k_i values cannot be increased significantly in the present systems, e.g., by increasing the phase ratio, because Joule heat generated during separation limits the concentration of the additives.

An increase of the capacity factors in the sequence TMA<TEA<DMP<PDADMA is found. It is obvious that this increase must stem from the increasing association constants, as the phase ratio, q, even decreases in this sequence.

In principle, in addition to the retention of the analytes by the additives in solution, another possible effect must be taken into account, namely the interaction with the polymer adsorbed at the capillary surface, the classical chromatographic mechanism. The magnitude of this effect can be evaluated in a BGE without additive. As a result it was found for nearly all analytes that the migration times could not be differentiated in the additive-free systems from

Table 2
Capacity factors, k_i, in 4% (w/w) solutions of the additives[a]

No.	Analyte	k_i			
		PDADMA	TMA	TEA	DMP
1	1,3-Dinitrobenzene	0.183	0.021	0.034	0.073
2	1,4-Naphthoquinone	0.188	0.034	0.053	0.141
3	Benzyl alcohol	0.200	0.056	0.064	0.122
4	2-Nitrobenzaldehyde	0.204	0.031	0.049	0.177
5	Benzophenone	0.272	0.087	0.101	0.270
6	1-Naphthaldehyde	0.346	0.136	0.156	0.373
7	Hydroquinone	0.405	0.114	0.128	0.284
8	Resorcinol	0.481	0.149	0.142	0.313
9	2-Naphthol	0.658	0.186	0.206	0.396
10	1-Naphthol	0.799	0.216	0.221	0.407

[a] Phase ratio, q: TMA, 0.00650; TEA, 0.00430; DMP, 0.00472; PDADMA, 0.00476. The reproducibility, expressed by the span of the measurements in duplicate, was between 1 and 5% for TMA and TEA, less than 10% for PDADMA and typically between 15 and 20% for DMP.

those of the EOF marker (the water dip) and therefore no retention is observable. Only 1-naphthol and 2-naphthol (the components with large interaction with the polymer) show retardation. This effect contributes to the capacity factors with a value of 0.063 for 1-naphthol, and 0.048 for 2-naphthol, both determined in the additive-free BGE with PDADMA coated at the capillary wall. It must be concluded that this effect might add a certain contribution to the retention for these two analytes (given that it takes place to the same extent in the systems containing additives in solution).

3.2. Association constant

The association constants, K_i, calculated from Eq. (7) are given in Fig. 3 for the analytes in all four systems. In the polymeric additive system the association constants are between 50 and 170, in accordance with our previous papers [43,44]. The values of K_i are in general smaller for the monomeric additives; they are increasing in the sequence TMA<TEA<DMP. However, a change in selectivity can be seen from the plots, especially for the analytes 1-naphthaldehyde (6) and hydroquinone (7) in the DMP and PDADMA systems.

3.3. Retention window

The principle question whether a larger retention window can be established with a polymeric additive or not, compared to a monomeric additive with the same initial mobility, is of main significance. It is an important matter because the span of the retention window determines the number of separable compounds (the peak efficiency is the other decisive quantity in this respect).

First we concentrate the discussion on the conditions when the direction of the EOF and the additive are opposite, and the real mobility of the additive is not larger than that of the EOF (as a limiting case we take μ^0_{add} equal to μ_{eof}). It is obvious that the maximum retention window is formed between an analyte with capacity factor zero, which will be eluted first (with the mobility of the EOF) and the last eluting component, *z*. If this component has a capacity factor of infinity, it has infinite retention time. However, the retention window is not necessarily infinite for the special case that $\mu^0_{(z+add)}$ equals μ_{eof}, as only a fraction of analyte might be associated with the additive.

For the comparison of polymeric or monomeric additives we assume for simplicity that μ^0_{add} for both additives is equal (there is no reason to take μ^0_{add} of

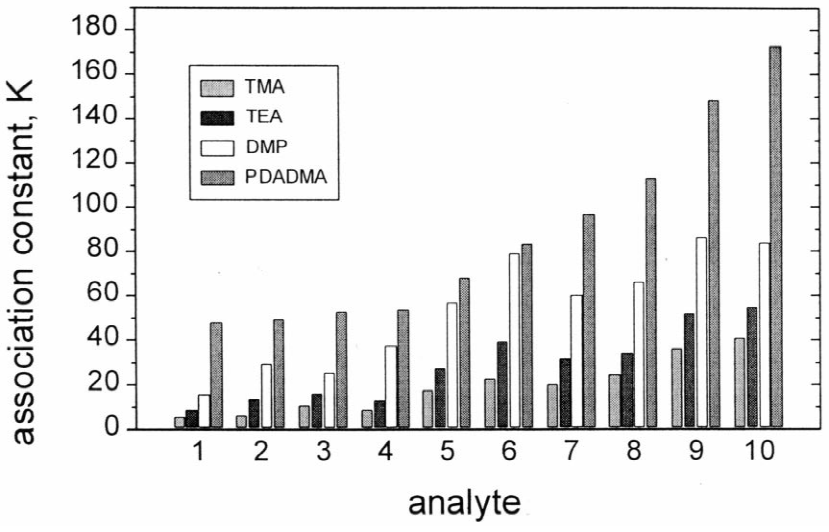

Fig. 3. Association constants, K_i, of the analytes in the systems with the different additives. Numbering of the analytes as in Table 1.

the one additive a priori larger or smaller than the other). There is also no preference for either a larger or a smaller mobility of the EOF compared to μ^0_{add}. Indeed both cases were observed for the present systems, as can be seen from the following values of the mobilities (all $\cdot 10^{-9}$ m^2 V^{-1} s^{-1}) derived for 4% (w/w) solutions of the polymer or the monomers, respectively. PDADMA: 38.4, EOF 32.2; TMA 28.3, EOF 21.7; TEA 18.7, EOF 23.4 (it should be mentioned that the variation of the EOF is obvious, because the systems exhibit different ionic strengths, and dynamic coating of the wall by the particular additives most probably occurs as well).

For a general comparison we presume that a monomer as additive will lead to a reduction of the mobility of the associate compared to that of the additive, in contrast to a polymeric one. Thus a reduction of the retention window will result. Indeed it was found that the $\mu^0_{(z+add)}$ values under consideration are between 1/4 and 3/4 of μ^0_{add} of the monomeric additives. From this point of view the application of a polymer is preferable over a monomer with comparable initial mobility.

An illustration of this effect is given in Fig. 4, where the separation of three analytes (benzyl alcohol, resorcinol and 2-naphthol) in the systems with PDADMA and TEA, respectively, is shown. In addition to the principal advantage, all other parameters favour the use of the polymer compared to the monomeric additive, too: the mobility of the EOF is higher, the capacity factors are higher, and the polymer has the highest real mobility of all additives. As result the largest retention window is observed for the PDADMA additive.

There is a small range where the application of the monomer might be favourable: at high μ^0_{add} com-

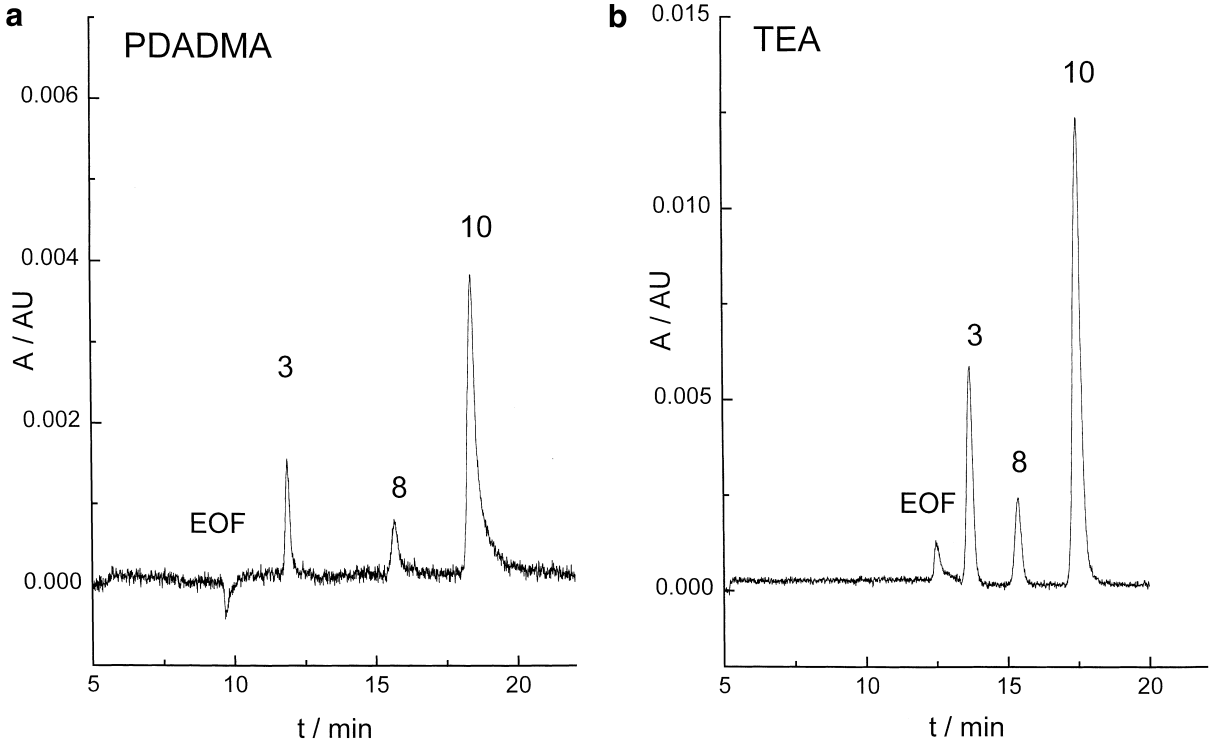

Fig. 4. Separation of a mixture of benzyl alcohol, resorcinol and 2-naphthol in the systems with the polymeric (PDADMA) (a) and a monomeric additive (TEA) (b). Additive concentration: 4% (w/w). Numbers of analytes as in Table 1. Conditions: PDADMA-coated capillary [27.0 cm (effective length 20.0 cm)×50 μm I.D.]; pressurized injection 2 s/35 mbar; temperature 25°C; voltage −3 kV; current 46 μA (PDADMA) and 64 μA (TEA); UV absorbance detector (214 nm) placed at the anodic end of the capillary.

pared to μ_{eof}, and at an unusually small difference between the μ^0_{add} and $\mu^0_{(z+add)}$. In such rare cases the retention window might be enlarged by the use of the monomeric additive after reversal of the polarity [71].

4. Concluding remarks

(i) Monomeric additives with the same quaternary ammonium functionality introduce retention into the electrokinetic system, similarly to the polymeric additive. The extend of interaction (expressed by the association constant) is smaller for the monomers, and follows the sequence TMA<TEA<DMP. This is not the sequence of increasing alkyl substitution, because DMP has less CH_2 groups than TEA. For some analytes the association constants for DMP nearly reach those of the polymer. It is noticeable that both, DMP and PDADMA, have the quaternary ammonium in the same five-ring structure (see Fig. 1).

(ii) The separation selectivity is similar for all systems. However, changes in selectivity occur. One pronounced example is the pair 1-naphthaldehyde (6) and hydroquinone (7), where the selectivity change in the systems with PDADMA and TEA, respectively, leads to clear baseline separation with reversed migration order of these two analytes.

(iii) The retention window is larger using polymeric additives compared to the monomeric ones (with the same initial mobility of additive species) in most practical cases. This fact results from the reduction of the mobility of the analyte–additive associate in case of the monomers, whereas for the polymers this effect is neglible (similar to micelles in MEKC).

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References

[1] H. Ozaki, S. Terabe, A. Ichihara, J. Chromatogr. A 680 (1994) 117.
[2] H. Ozaki, A. Ichihara, S. Terabe, J. Chromatogr. A 709 (1995) 3.
[3] M. Aguilar, A. Farran, C. Serra, M.J. Sepaniak, K.W. Whitaker, J. Chromatogr. A 778 (1997) 201.
[4] H. Ozaki, N. Itou, S. Terabe, Y. Takada, M. Sakairi, H. Koizumi, J. Chromatogr. A 716 (1995) 69.
[5] H. Ozaki, S. Terabe, J. Chromatogr. A 794 (1998) 317.
[6] S.K. Wiedmer, H. Tenhu, P. Vastamäki, M.-L. Riekkola, J. Microcol. Sep. 10 (1998) 557.
[7] S. Yang, J.G. Bumgarner, M.G. Khaledi, J. High Resolut. Chromatogr. 18 (1995) 443.
[8] S. Yang, J.G. Bumgarner, M.G. Khaledi, J. Chromatogr. A 738 (1996) 265.
[9] N. Tanaka, K. Nakagawa, H. Iwasaki, K. Hosoya, K. Kimata, T. Araki, D.G. Patterson Jr., J. Chromatogr. A 781 (1997) 139.
[10] N. Tanaka, K. Nakagawa, K. Hosoya, C.P. Palmer, S. Kunugi, J. Chromatogr. A 802 (1998) 23.
[11] N. Tanaka, K. Nakagawa, H. Nagayama, K. Hosoya, T. Ikegami, A. Itaya, M. Shibayama, J. Chromatogr. A 836 (1999) 295.
[12] S.A. Shamsi, J. Macossay, I.M. Warner, Anal. Chem. 69 (1997) 2980.
[13] K.A. Agnew-Heard, M. Sanchez Pena, S.A. Shamsi, I.M. Warner, Anal. Chem. 69 (1997) 958.
[14] C. Akbay, I.M. Warner, S.A. Shamsi, Electrophoresis 20 (1999) 145.
[15] E. Billiot, J. Macossay, S. Thibodeaux, S.A. Shamsi, I.M. Warner, Anal. Chem. 70 (1998) 1375.
[16] E. Billiot, R.A. Agbaria, S. Thibodeaux, S. Shamsi, I.M. Warner, Anal. Chem. 71 (1999) 1252.
[17] E. Billiot, S. Thibodeaux, S. Shamsi, I.W. Warner, Anal. Chem. 71 (1999) 4044.
[18] F. Haddadian, S.A. Shamsi, I.M. Warner, Electrophoresis 20 (1999) 3011.
[19] C.P. Palmer, M.Y. Khaled, H.M. McNair, J. High Resolut. Chromatogr. 15 (1992) 756.
[20] C.P. Palmer, S. Terabe, Anal. Chem. 69 (1997) 1852.
[21] C.P. Palmer, J. Chromatogr. A 780 (1997) 75.
[22] C.P. Palmer, N. Tanaka, J. Chromatogr. A 792 (1997) 105.
[23] S.A. Shamsi, C. Akbay, I.M. Warner, Anal. Chem. 70 (1998) 3078.
[24] H.H. Yarabe, S.A. Shamsi, I.M. Warner, Anal. Chem. 71 (1999) 3992.
[25] J. Wang, I.M. Warner, Anal. Chem. 66 (1994) 3773.
[26] M. Castagnola, L. Cassiano, A. Lupi, I. Messana, M. Patamia, R. Rabino, D.V. Rossetti, B. Giardina, J. Chromatogr. A 694 (1995) 463.
[27] P.G.H.M. Muijselaar, H.A. Claessens, C.A. Cramers, J.F.G.A. Jansen, E.W. Meijer, E.M.M. de Brabander-van den Berg, S. van der Wal, J. High Resolut. Chromatogr. 18 (1995) 121.

[28] N. Tanaka, T. Fukutome, T. Tanigawa, K. Hosoya, K. Kimata, T. Araki, K.K. Unger, J. Chromatogr. A 699 (1995) 331.
[29] N. Tanaka, T. Fukutome, K. Hosoya, K. Kimata, T. Araki, J. Chromatogr. A 716 (1995) 57.
[30] S.A. Kuzdzal, C.A. Monnig, G.R. Newkome, C.N. Moorefield, J. Am. Chem. Soc. 119 (1997) 2255.
[31] H. Gao, J. Carlson, A.M. Stalcup, W.R. Heineman, J. Chromatogr. Sci. 36 (1998) 146.
[32] A.L. Gray, J.T. Hsu, J. Chromatogr. A 824 (1998) 119.
[33] C. Stathakis, E.A. Arriaga, N.J. Dovichi, J. Chromatogr. A 817 (1998) 233.
[34] N. Tanaka, H. Iwasaki, T. Fukutome, K. Hosoya, T. Araki, J. High Resolut. Chromatogr. 20 (1997) 529.
[35] M. Sanchez Pena, Y. Zhang, I.M. Warner, Anal. Chem. 69 (1997) 3239.
[36] S. Sun, M.J. Sepaniak, J.-S. Wang, C.D. Gutsche, Anal. Chem. 69 (1997) 344.
[37] D. Shohat, E. Grushka, Anal. Chem. 66 (1994) 747.
[38] K. Bächmann, A. Bazzanella, I. Haag, K.-Y. Han, R. Arnecke, V. Böhmer, W. Vogt, Anal. Chem. 67 (1995) 1722.
[39] A. Bazzanella, H. Mörbel, K. Bächmann, R. Milbradt, V. Böhmer, W. Vogt, J. Chromatogr. A 792 (1997) 143.
[40] A. Bazzanella, K. Bächmann, R. Milbradt, V. Böhmer, W. Vogt, Electrophoresis 20 (1999) 92.
[41] B. Maichel, B. Potocek, B. Gas, M. Chiari, E. Kenndler, Electrophoresis 19 (1998) 2124.
[42] B. Maichel, B. Potocek, B. Gas, E. Kenndler, J. Chromatogr. A 853 (1999) 121.
[43] B. Maichel, B. Gas, E. Kenndler, Electrophoresis, in press.
[44] B. Potocek, E. Chmela, B. Maichel, E. Tesarova, E. Kenndler, B. Gas, Anal. Chem. 72 (2000) 74.
[45] F.B. Erim, J. Chromatogr. A 768 (1997) 161.
[46] S. Terabe, T. Isemura, J. Chromatogr. 515 (1990) 667.
[47] S. Terabe, T. Isemura, Anal. Chem. 62 (1990) 650.
[48] C. Stathakis, R.M. Cassidy, Anal. Chem. 66 (1994) 2110.
[49] C. Stathakis, R.M. Cassidy, J. Chromatogr. A 699 (1995) 353.
[50] A. Cifuentes, H. Poppe, J.C. Kraak, F.B. Erim, J. Chromatogr. B 681 (1996) 21.
[51] S. Honda, K. Togashi, K. Uegaki, A. Taga, J. Chromatogr. A 805 (1998) 277.
[52] T.W. Garner, E.S. Yeung, J. Chromatogr. 640 (1993) 397.
[53] W.D. Pfeffer, E.S. Yeung, J. Chromatogr. 557 (1991) 125.
[54] O. Brüggemann, R. Freitag, J. Chromatogr. A 717 (1995) 309.
[55] C.M. Knapp, J.J. Breen, J. Chromatogr. A 799 (1998) 289.
[56] D. Crosby, Z. El Rassi, J. Liq. Chromatogr. 16 (1993) 2161.
[57] A. Dworschak, U. Pyell, J. Chromatogr. A 848 (1999) 387.
[58] A. Dworschak, U. Pyell, J. Chromatogr. A 855 (1999) 669.
[59] Y. Walbroehl, J.W. Jorgenson, Anal. Chem. 58 (1986) 479.
[60] P.G. Muijselaar, H.B. Verhelst, H.A. Claessens, C.A. Cramers, J. Chromatogr. A 764 (1997) 323.
[61] Y. Shi, J.S. Fritz, J. High Resolut. Chromatogr. 17 (1994) 713.
[62] S. Pedersen-Bjergaard, K.E. Rasmussen, T. Tilander, J. Chromatogr. A 807 (1998) 285.
[63] O. Naess, T. Tilander, S. Pedersen-Bjergaard, K.E. Rasmussen, Electrophoresis 19 (1998) 2912.
[64] J. Tjornelund, S.H. Hansen, J. Chromatogr. A 792 (1997) 475.
[65] Y. Shi, J.S. Fritz, Anal. Chem. 67 (1995) 3023.
[66] W. Ding, J.S. Fritz, Anal. Chem. 69 (1997) 1593.
[67] W. Ding, J.S. Fritz, Anal. Chem. 70 (1998) 1859.
[68] Landolt-Börnstein Zahlenwerke und Funktionen aus Naturwissenschaft und Technik, Springer-Verlag, Berlin, 1969.
[69] E. Kenndler, P. Jenner, J. Chromatogr. 390 (1987) 185.
[70] J.F. Bunnett, S. Sekiguchi, L.A. Smith, J. Am. Chem. Soc. 103 (1981) 4865.
[71] J.P. Quirino, S. Terabe, J. Chromatogr. A 856 (1999) 465.