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Optimization of the separation of polycarboxylic acids by capillary zone electrophoresis

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Abstract

The optimization of electrolyte systems for the separation and detection of polycarboxylic acids using capillary zone electrophoresis is described. A borate buffer in the pH range 9–10 was chosen for the separation. The factors affecting separation selectivity include the addition of complexing reagents, such as alkaline earth metal ions and cyclodextrins, to the carrier electrolyte. A model can be developed that is based on the chemical complexation equilibria and allows the prediction of migration times and optimum carrier electrolyte compositions. Five experiments were found to be sufficient for establishing optimum separation conditions for 18 di- and tricarboxylic acids. UV detection at 185 nm was feasible for both aromatic and aliphatic carboxylic acids. The technique can be applied to the determination of the carboxylic acid composition of alkyd resins and similar technical products.

Keywords: Optimization; Buffer composition; Polycarboxylic acids; Carboxylic acids

1. Introduction

Polycarboxylic acids are used extensively for manufacturing of a broad range of technical products and large amounts are used for the synthesis of various resins. Quality control procedures of these products require reliable analytical methods. Carboxylic acids in resins can be analyzed after alkaline hydrolysis. Traditionally, gas chromatography (GC) has been used for the determination of carboxylic acids. This technique suffers from the fact that carboxylic acids are often not suited for direct GC analysis but must be derivatized to enhance the volatility. Attempts to overcome some drawbacks of GC have led to an increased interest in separation methods in the liquid phase instead of the gas phase. During recent years, ion chromatography (IC) both in the form of ion-exchange and ion-exclusion chromatography has emerged as an attractive technique for the separation of organic acids. Unfortunately, the separation efficiency of IC is considerably lower than that of GC.

Currently, capillary zone electrophoresis (CZE) is growing in significance as an analytical technique for the separation of low-molecular-mass ionic species. It appears to be an attractive complementary technique to ion chromatography with promising features such as high separation efficiency, short analysis time and unique separation selectivity. CZE separation procedures for a variety of organic acids are already well documented in the literature [1–8]. Generally, low-molecular-mass carboxylic acids are separated in a coelectroosmotic mode with indirect UV detection. Coelectroosmotic CZE of anionic species can only be carried out if the direction of the electroosmotic flow is reversed and directed to the anode. This reversal can be accomplished by the addition of hydrophobic quaternary ammonium ions

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to the carrier electrolyte [9,10]. Electrolytes reported for indirect UV detection include benzoate and phthalate [1,3], hydroxybenzoate and sorbate [5,11], pyromellitate [10], naphthalenedicarboxylic acid [7], naphthalenesulfonates [6] and *p*-aminobenzoate [8]. Direct UV detection can be employed for aromatic carboxylic acids [2] and even for aliphatic carboxylic acids at 185 nm as demonstrated recently by Shirao et al. [4]. Direct UV detection seems to be favorable due to a better stability of the baseline.

Despite the fact that several applications of CZE for the determination of carboxylic acids do already exist, the potential of CZE for the analysis of carboxylic acids in technical products and the possibilities of optimizing the separation conditions have not yet been fully exploited. As far as resin composition analysis is concerned, the only paper published so far seems to be that of McNair and Sun [12], who analyzed polycarboxylic acids in polyimide samples. The aim of the work presented in this paper was the separation of a range of polycarboxylic acids (mainly dicarboxylic acids) that are relevant for alkyd resins. Different approaches to the optimization of separation selectivity have been investigated in detail. Finally, a migration model has been developed that is based on equilibria between the analytes and complexing reagents in the carrier electrolyte. This model should allow a rapid computer-assisted optimization of the CZE separation.

2. Experimental

2.1. Instrumentation

The CZE instrument employed was a Quanta 4000 (Waters, Milford, MA, USA) equipped with a negative power supply and a fixed-wavelength detector at 185 nm (mercury lamp) which was interfaced to a HP 3359 data acquisition system (Hewlett Packard, Palo Alto, CA, USA). Separations were carried out using fused-silica capillaries obtained from Polymicro Technologies (Phoenix, AZ, USA) with effective lengths between 48 and 70 cm, inner diameters of 75 μm and a detection window at a position of 8 cm from the end. Injection was performed hydrostatically at the cathodic side by elevating the sample at 10 cm for a specified time. Direct UV detection at 185 nm was used.

SigmaPlot software (Jandel Scientific, Erkrath, Germany) was employed for the calculations during optimization of the carrier electrolyte composition.

2.2. Carrier electrolytes

The carrier electrolytes consisted of 25 m*M* sodium tetraborate containing 0.5 m*M* tetradecyltrimethylammonium bromide (TTAB) and varying concentrations of strontium, calcium or barium salts as well as α-cyclodextrin (Sigma, St. Louis, MO, USA), β-cyclodextrin (Fluka, Buchs, Switzerland) or γ-cyclodextrin (Sigma). All carrier electrolytes were prepared from analytical-reagent grade chemicals using double distilled water.

2.3. Polycarboxylic acids

The following carboxylic acids of highest purity available were used: oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, fumaric acid, *trans*-1,4-cyclohexanedicarboxylic acid, potassium hydrogenphthalate, isophthalic acid (all obtained from Merck, Darmstadt, Germany), pimelic acid, *cis*-1,2-cyclohexanedicarboxylic anhydride, *trans*-1,2-cyclohexanedicarboxylic anhydride, mixture of *cis*- and *trans*-1,4-cyclohexanedicarboxylic acid, terephthalic acid disodium salt, 1,3,5-benzenetricarboxylic acid, 1,2,4-benzenetricarboxylic acid (all obtained from Aldrich, Vienna, Austria), maleic anhydride (obtained from Chemie Linz, Linz, Austria).

3. Results and discussion

3.1. Parameters for optimization of separation selectivity

Throughout this work direct UV detection at 185 nm was used. This detection mode limits the number of suitable carrier electrolytes. Initial experiments on optimization of separation selectivity were performed employing phosphate buffers in a pH range of 5–8 and borate buffers in a pH range of 8–11 as the carrier electrolyte. All electrolytes contained 0.5 m*M*

TTAB in order to reverse the electroosmotic flow and to establish coelectroosmotic separation conditions. The results indicated that some of the dicarboxylic acids exhibited poor peak shapes when an acidic carrier electrolyte was employed. Therefore, an alkaline borate buffer or sodium tetraborate were employed for all further experiments.

In a borate buffer, several dicarboxylic acids were found to exhibit similar ionic mobilities so that a complete separation was not possible. Generally, the ion mobilities can be manipulated by: organic solvents affecting the solvation [13,14]; pH affecting the dissociation and thereby the charge of weak acids or bases [15–17]; complexing reagents affecting the charge.

The only organic solvent that was sufficiently UV transparent at 185 nm and miscible with water was acetonitrile. The separation selectivity could be slightly improved by the addition of acetonitrile to the carrier electrolyte. At the same time, the analysis time was increased due to a decreased electroosmotic flow. Unfortunately, the volatility of acetonitrile is high enough to cause serious changes of the composition of the carrier electrolyte in the electrolyte vials during a series of runs. As a result, the reproducibility was poor, so that the use of acetonitrile for the optimization of separation selectivity was not further investigated.

Results from the literature [15–17] indicate that pH variation can be a powerful tool for manipulation of migration times and separation selectivity. Nevertheless, some of the carboxylic acids included in this study yielded poor peak shapes under acidic pH conditions (see above), so that carrier electrolytes buffered in the range of pK values of the dicarboxylic acids could not be employed.

The most promising approach to the optimization of separation selectivity turned out to be the addition of complexing reagents to the carrier electrolyte. It is well known that alkaline earth cations can form weak complexes with various dicarboxylic acids. The addition of calcium ions has been reported to improve the separation of organic acids in sugar refinery juices [3]. Within the present work, the use of calcium, strontium and barium ions (chloride or nitrate salts) was investigated. The complex formation of calcium or strontium ions was found to be slightly too strong with some acids, especially with oxalic acid. Therefore, barium ions were chosen for all further work. The addition of barium ions as their chloride or nitrate salts resulted in an unfavorable increase in UV absorption of the carrier electrolyte. For this reason, UV transparent barium hydroxide was employed causing a slight increase in pH. The influence of these pH changes on the separation was negligible. One should be aware of the fact that in the case of the widely used indirect UV detection the addition of barium ions would lead to a decrease in sensitivity due to the decreased effective charge [18], whereas direct UV detection as described in this paper is practically not affected.

The presence of barium ions in the carrier electrolyte allowed considerably improved separations of the carboxylic acids included in this study. As can be seen from Fig. 1, pronounced effects were observed for oxalic acid, maleic acid, 1,2,4-benzenetricarboxylic acid, *o*-phthalic acid and *cis*-1,2-cyclohexanedicarboxylic acid (that are those compounds that contain two vicinal carboxylate groups in a steric position allowing the complexation with barium ions; therefore, maleic acid is strongly affected, whereas

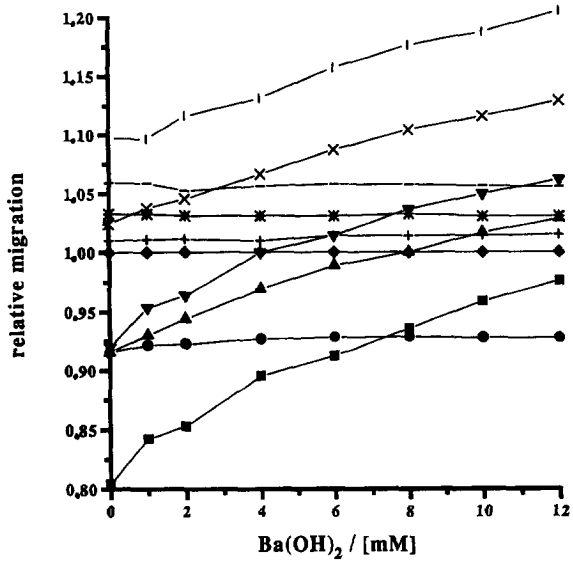

Fig. 1. Effect of barium hydroxide in the carrier electrolyte on the migration order relative to glutaric acid. ■ = Oxalic acid; ● = fumaric acid; ▲ = maleic acid; ▼ = 1,2,4-benzenetricarboxylic acid; ◆ = glutaric acid; + = terephthalic acid; × = *o*-phthalic acid; * = adipic acid; – = pimelic acid; | = *cis*-1,2-cyclohexanedicarboxylic acid.

fumaric acid not at all). Nevertheless, a complete separation of all analytes was not yet possible. The incorporation of a second complexing reagent into the carrier electrolyte seemed necessary. Our search for selective complexing reagents for various carboxylic acids led to investigations on cyclodextrins. In CZE, cyclodextrins are commonly used for the separation of enantiomers. Recently, cyclodextrins have also been reported for improving the separation of inorganic anions such as chloride and iodide [14] due to the formation of inclusion complexes. Cyclodextrins have not yet been used for fine-tuning of separation selectivity of carboxylic acids in CZE, although their benefits are known from ion-exclusion chromatography [19], where β-cyclodextrin can reduce the retention times of aromatic carboxylic acids. Both α-, β- and γ-cyclodextrins were used within this study. Best results could be obtained with β-cyclodextrin.

Both the addition of barium ions and cyclodextrin exerted a significant influence on the electroosmotic flow. Cyclodextrin can compensate the effect of TTAB and reestablishes a cathodic electroosmotic flow. This effect might be explained by some tendency of cyclodextrin to form inclusion complexes with TTAB, thereby reducing its effective concentration. On the other hand, the addition of barium ions to an electrolyte containing cyclodextrin reduces the cathodic electroosmotic flow. This effect of barium ions is in agreement with results reported recently [20] for di- and trivalent cations. Electrostatic interactions of these ions with the negative charge at the inner surface of the capillary decrease the zeta-potential and thereby the electroosmotic flow. The dependence of the electroosmotic flow on the concentration of cyclodextrin at different barium concentrations is shown in Fig. 2. A coelectroosmotic separation mode was no longer possible and somewhat longer analysis times had to be accepted.

An optimized separation of all carboxylic acids included in this study is shown in Fig. 3. The optimization of this electropherogram was done by trial and error. This optimization procedure is time-consuming and does not guarantee that the separation achieved is really the optimum. A more systematic optimization seemed highly desirable. Yang et al. [21] have reported the development of a migration model for inorganic cations in a carrier electrolyte containing 2-hydroxyisobutyric acid and 18-crown-6 as complexing agents. This migration model has allowed the systematic optimization of the CE separation of twelve cations. The development of a similar model for the separation of carboxylic acids seemed to be a promising approach and is described below.

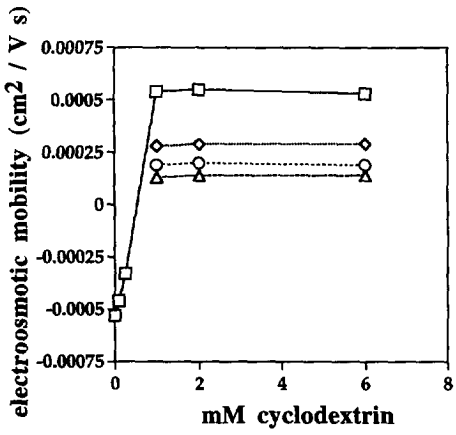

Fig. 2. Dependence of the electroosmotic mobility on the concentration of β-cyclodextrin and barium hydroxide. □=0 m*M* Ba, ◇=2 m*M* Ba, ○=4 m*M* Ba, △=6 m*M* Ba.

3.2. Model for the migration of carboxylic acids in the presence of complexing reagents

The effective electrophoretic mobility μ_{eff} of a carboxylate anion in the presence of barium ions and cyclodextrin is the sum of the mobility of the free carboxylate anion (μ_A), the mobility of the barium–carboxylate complex (μ_{BA}) and the mobility of the cyclodextrin–carboxylate complex (μ_{CA}), each multiplied by the respective molar fraction α:

$$\mu_{eff} = \mu_A \alpha_A + \mu_{BA} \alpha_{BA} + \mu_{CA} \alpha_{CA} \quad (1)$$

Expressions for the molar fractions can be obtained in a way analogous to that reported in the literature for the separation of cations [21,22] by using the complex formation constants K_{BA} for the barium–carboxylate complex and K_{CA} for the cyclodextrin–carboxylate complex (c_A = concentration of the free carboxylate anion, c_B = concentration of barium ions, c_C = concentration of cyclodextrin):

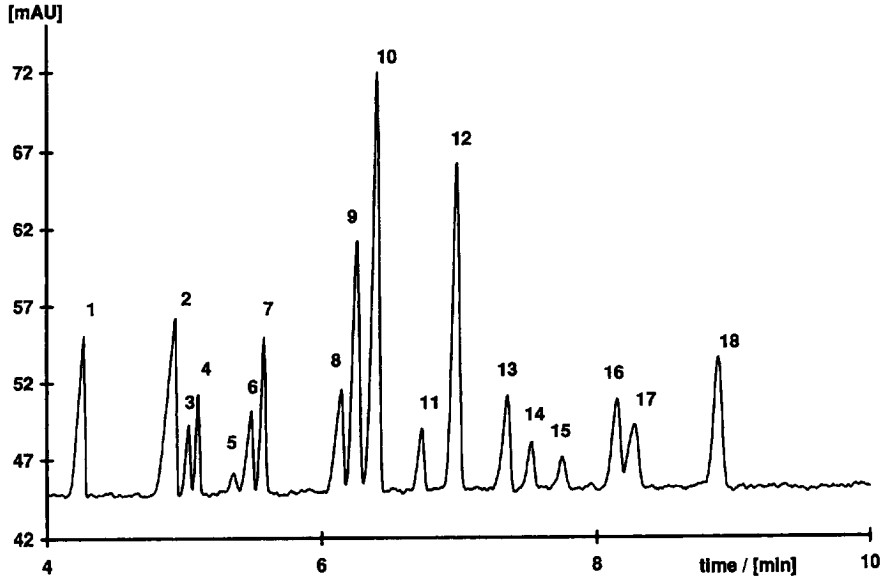

Fig. 3. Electropherogram of a mixture of carboxylic acid. Carrier electrolyte: 25 m*M* sodium tetraborate containing 0.5 m*M* TTAB, 2 m*M* β-cyclodextrin and 2.25 m*M* barium hydroxide; voltage: −12 kV; injection time: 20 s; detection: direct UV at 185 nm; capillary: 48 cm×75 μm I.D. Peaks: 1 = oxalic acid; 2 = malonic acid; 3 = fumaric acid; 4 = 1,3,5-benzenetricarboxylic acid; 5 = maleic acid; 6 = succinic acid; 7 = 1,2,4-benzenetricarboxylic acid; 8 = glutaric acid; 9 = isophthalic acid; 10 = terephthalic acid; 11 = adipic acid; 12 = *o*-phthalic acid; 13 = pimelic acid; 14 = *cis*-1,4-cyclohexanedicarboxylic acid; 15 = *trans*-1,4-cyclohexanedicarboxylic acid; 16 = suberic acid; 17 = *trans*-1,2-cyclohexanedicarboxylic acid; 18 = *cis*-1,2-cyclohexanedicarboxylic acid.

$$\alpha_A = \frac{c_A}{c_{total}} = \frac{c_A}{c_A + K_{BA}c_Ac_B + K_{CA}c_Ac_C} = \frac{1}{1 + K_{BA}c_B + K_{CA}c_C} \quad (2)$$

$$\alpha_{BA} = \frac{c_{BA}}{c_{total}} = \frac{c_{BA}}{c_A + K_{BA}c_Ac_B + K_{CA}c_Ac_C} = \frac{K_{BA}c_B}{1 + K_{BA}c_B + K_{CA}c_C} \quad (3)$$

$$\alpha_{CA} = \frac{c_{CA}}{c_{total}} = \frac{c_{CA}}{c_A + K_{BA}c_Ac_B + K_{CA}c_Ac_C} = \frac{K_{CA}c_C}{1 + K_{BA}c_B + K_{CA}c_C} \quad (4)$$

The combination of Eqs. 1–4 yields the expression for the effective mobility:

$$\mu_{eff} = \frac{\mu_A + \mu_{BA}K_{BA}c_B + \mu_{CA}K_{CA}c_C}{1 + K_{BA}c_B + K_{CA}c_C} \quad (5)$$

The charge of a complex of barium with dicarboxylate anions is zero, so that the mobility μ_{BA} is zero. For samples containing only dicarboxylic acids, Eq. 5 can be reduced to the following expression:

$$\mu_{eff} = \frac{\mu_A + \mu_{CA}K_{CA}c_C}{1 + K_{BA}c_B + K_{CA}c_C} \quad (6)$$

Values for μ_A, μ_{BA}, μ_{CA}, K_{BA} and K_{CA} can be obtained from a limited number of experiments. Once these values are known, Eq. 5 can be used for prediction of migration times and for computer-assisted optimization of separation selectivity.

The equilibria taken into account in the model are not necessarily the only equilibria present in the system. Among others, there can be interactions between TTAB and cyclodextrin as mentioned above as well as interactions between TTAB and carboxylate anions resulting in the formation of ion pairs. Obviously, it can get difficult to specify all equilibria in an exact way. A way around this problem has been shown by Corstjens et al. [23] who assumed a linear relationship between the migration

of each analyte and the parameters examined. This allows a first approximation of the best separation conditions. Additional experiments are then carried out in an iterative manner to refine the linear model. Unfortunately, there is the disadvantage that one might reach just a local instead of a global optimum, especially if the parameter space is very large. Therefore, we tried to use a model that is as close as possible to the reality without being too complex and to refine the results in an iterative way if necessary. In this case, there is less risk of missing the global optimum and the number of necessary iterations is smaller.

3.3. Computer-assisted optimization of separation selectivity

The optimization process requires the selection of sensible upper and lower limits for the parameters c_B, c_C to be optimized. This selection was done on the basis of some general knowledge available on the behavior of carboxylic acids. The upper limits of the parameter space was set to 6 m*M* cyclodextrin and 6 m*M* barium, whereas the lower limits were set to zero.

The start of the optimization procedure consisted of five experimental runs done at the following locations within the parameter space: one run was carried out at each corner of the parameter space (experiments 1–4) and one was carried out in the middle of the parameter space (experiment 5). The effective electrophoretic mobilities of the carboxylic acids were calculated from the observed migration times as follows:

$$\mu_{eff} = \frac{L_T L_D}{U}\left(\frac{1}{t_m} - \frac{1}{t_0}\right) \quad (7)$$

L_T and L_D are the total length of the capillary and the length between injection point and detection point, respectively; U is the separation voltage; t_m and t_0 are the migration times of the carboxylic acid and of benzyl alcohol as a neutral marker, respectively.

The experimental data could be used for non-linear regression calculations to obtain values for the parameters of Eq. 5. Finally, Eq. 5 allowed the prediction of separations. The minimum difference in effective electrophoretic mobilities of two adjacent peaks in a predicted electropherogram was used as an optimization criterion. Although other criteria might be more efficient in describing the resolution of two electrophoretic peaks, the criterion of minimum difference in mobility is attractive due to its simplicity and has been successfully used in the systematic optimization of CE conditions for inorganic cations and anions [21,24,25]. A computer program written in BASIC was used to find the maximum of this criterion.

The predicted optimum was verified by an additional experimental run (experiment 6). In case this experimental run differed too much from the predicted run, the linear regression calculation was repeated using the data from experiment 6 and the data from four runs out of the experiments 1–5 (the data of the experiment that was most distant from experiment 6 in the parameter space was omitted). A new optimum was predicted and verified. If necessary, the optimization process was repeated until a satisfactory separation was obtained.

Our first results of this optimization procedure for carboxylic acids were disappointing. The non-linear regression calculation indicated that the data of the five experiments carried out at the beginning of the procedure did not properly fit to the model. Additional investigations revealed that the model was appropriate for all concentrations of cyclodextrin and barium except for the range of 0 to 1 m*M* cyclodextrin. One might explain this behavior by the above-mentioned tendency of cyclodextrin to form inclusion complexes with TTAB. At low concentrations of cyclodextrin the concentration of free TTAB might be high enough to form to some extent ion pairs with the carboxylate anions. Such an equilibrium has not been taken into account in our model. At cyclodextrin concentrations above 1 m*M*, the concentration of free TTAB decreases and the interactions of TTAB with carboxylate anions would become negligible, so that the model is appropriate. Therefore, the lower limit of cyclodextrin in the parameter space was set to 1 m*M*. For practical purposes, this is not a serious limitation, because the influence of cyclodextrin at concentrations below 1 m*M* is too low to cause significant changes in the selectivity. Concentrations of barium below 2 m*M* would also be too low to be of any use for the

optimization procedure, so that its lower limit was set to 2 m*M*.

After changing the parameter space as described above, the calculated mobilities yielded an excellent correlation with the experimental mobilities (correlation coefficient better than 0.999). The predicted optimum electropherogram calculated from the experiments 1–5 was found at 2 m*M* cyclodextrin and 2.4 m*M* barium. It agreed reasonably well with the experimental result (experiment 6) and was close to the conditions found by trial and error (2 m*M* cyclodextrin, 2.25 m*M* barium, see above). A plot of the optimization criterion as a function of the concentrations of the complexing reagents is given in Fig. 4. This figure indicates that there is a second optimum at 3 m*M* cyclodextrin and 6 m*M* barium. Under these conditions, the separation selectivity is different (Fig. 5) but the value of the optimization criterion is similar. A continuation of the optimization procedure did not lead to a different optimum but always pointed to the same optimal conditions. In fact, the quality of the separation at these two points in the parameter space is practically the same. Table 1 shows the comparison of calculated and experimental mobilities at the two predicted optimum carrier electrolyte compositions. It can be concluded that 5 experiments are sufficient to achieve a satisfactory separation of the 18 carboxylic acids included in this study.

The method was used for the determination of the carboxylic acid composition of alkyd resin samples after hydrolysis. With this type of samples, no interferences were encountered. Determination limits were at 5 ppm in the sample solution. Admittedly, real alkyd resin samples will not contain the whole range of carboxylic acids included in this study. In some cases, a carrier electrolyte without any complexing reagents would be sufficient to separate the carboxylic acids of interest. On the other hand, real samples often require the analysis of some car-

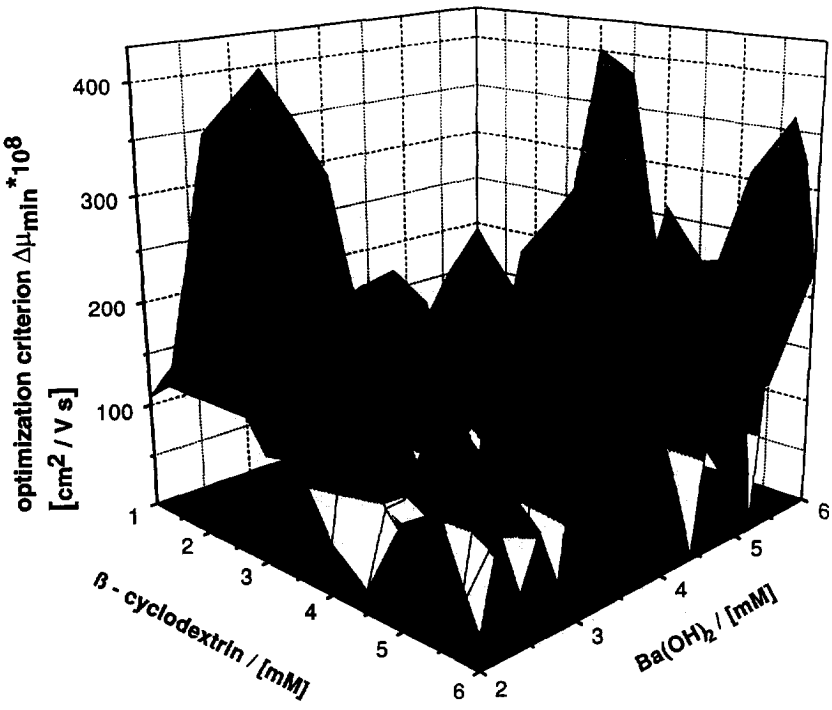

Fig. 4. Dependence of the optimization criterion on the concentration of barium hydroxide and β-cyclodextrin.

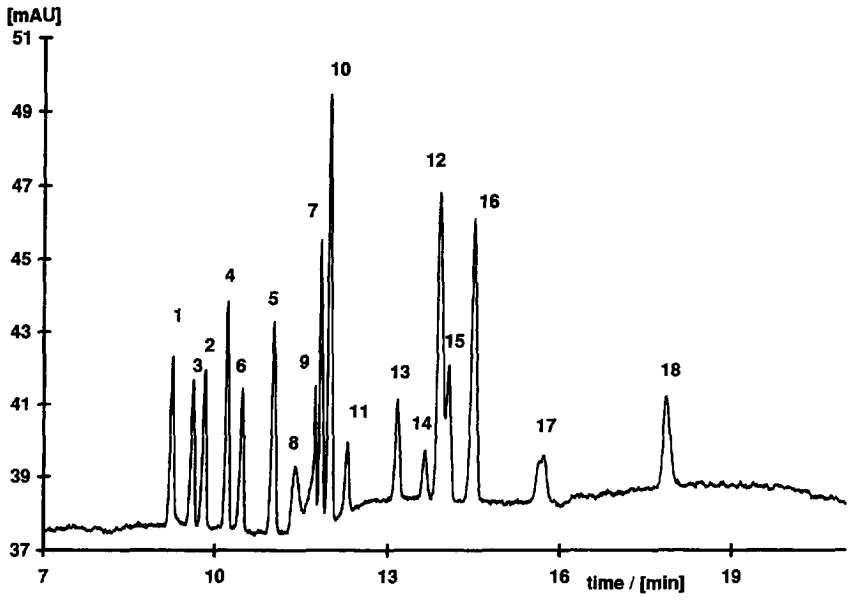

Fig. 5. Electropherogram of a mixture of carboxylic acid. Carrier electrolyte: 25 m*M* sodium tetraborate containing 0.5 m*M* TTAB, 3 m*M* β-cyclodextrin and 6 m*M* barium hydroxide; voltage: −10 kV; injection time: 20 s; detection: direct UV at 185 nm; capillary: 60 cm×75 μm I.D. Peak numbering as in Fig. 3.

boxylic acids in the presence of a large excess of other carboxylic acids. Simple separation conditions that work for carboxylic acids present at similar concentration levels might fail for such real samples. Therefore, even the analysis of a limited number of carboxylic acids necessitates maximum differences

Table 1
Comparison of predicted and measured mobilities at a carrier electrolyte composition of 3 m*M* cyclodextrin and 6 m*M* barium hydroxide (electrolyte 1) and 2 m*M* cyclodextrin and 2.4 m*M* barium hydroxide (electrolyte 2)

Carboxylic acid	μ(calculated)/μ(measured) ($cm^2V^{-1}s^{-1}$)·10^4	
	Electrolyte 1	Electrolyte 2
Oxalic acid	−5.16/−5.16	−5.70/−5.67
Fumaric acid	−5.00/−5.00	−5.07/−5.05
Malonic acid	−4.92/−4.92	−5.19/−5.17
1,3,5-Benzenetricarboxylic acid	−4.78/−4.77	−5.02/−5.00
Succinic acid	−4.69/−4.69	−4.78/−4.76
Maleic acid	−4.51/−4.51	−4.83/−4.81
Glutaric acid	−4.41/−4.41	−4.44/−4.43
Isophthalic acid	−4.31/−4.33	−4.36/−4.36
1,2,4-Benzenetricarboxylic acid	−4.28/−4.29	−4.69/−4.67
Terephthalic acid	−4.24/−4.24	−4.30/−4.30
Adipic acid	−4.17/−4.17	−4.17/−4.17
Pimelic acid	−3.97/−3.97	−3.96/−3.96
cis-1,4-Cyclohexanedicarboxylic acid	−3.87/−3.87	−3.89/−3.89
o-Phthalic acid	−3.82/−3.81	−4.07/−4.06
trans-1,4-Cyclohexanedicarboxylic acid	−3.79/−3.76	−3.82/−3.82
Suberic acid	−3.71/−3.70	−3.71/−3.72
trans-1,2-Cyclohexanedicarboxylic acid	−3.52/−3.52	−3.68/−3.67
cis-1,2-Cyclohexanedicarboxylic acid	−3.23/−3.23	−3.52/−3.52

in migration times between the analytes. These maximum differences can be easily found by the optimization procedures described above.

4. Conclusions

The results obtained in this work indicate that capillary zone electrophoresis is an attractive technique for the separation of various di- and tricarboxylic acids. High efficiencies and short analysis times are some of the advantages of this method compared with the well established technique of ion-exchange and ion-exclusion chromatography. The separation selectivity can be optimized for different applications by using barium ions and β-cyclodextrin. A model based on complexation equilibria between carboxylic acids and the complexing reagents enables the quick and efficient optimization of the carrier electrolyte composition. The data from five experiments were found to be sufficient for locating an optimum. It should be pointed out that the values for the parameters K_{BA} and K_{CA} obtained from the non-linear regression calculations are not necessarily accurate enough to be used as exact physicochemical constants for the respective complexation reaction. Nevertheless, they are good enough to be useful in the model presented in this paper. This fact indicates that the proposed model describes the chemical equilibria in the carrier electrolyte in a reasonably good but not completely exact way. The reasons for these deviations can be the complexation reaction between cyclodextrin and TTAB as well as the interactions of TTAB with carboxylate anions that have not been taken into account in the model. One might include these equilibria in a refined model, although such refinement seems to be unnecessary for practical purposes.

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