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Metal ion capillary electrophoresis with direct UV detection Effect of a charged surfactant on the migration behaviour of metal chelates

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Abstract

The migration behaviour of anionic metal 4-(2-pyridylazo)resorcinol (PAR) and Arsenazo III complexes was investigated in capillary electrophoresis (CE) using micellar solutions of sodium dodecyl sulphate. The separation mechanism of arsenazo complexes is governed by the electrophoresis in the bulk carrier electrolyte without any observable interaction with the micellar phase. For less hydrophilic PAR complexes, the resolution can be additionally explained in terms of differential partitioning into the micelle. It was also found that ion-pair formation between anionic solutes and the cationic component of the electrophoretic buffer contributes to the retention mechanism and permits the separation of closely migrating PAR complexes. Both chelating systems have been applied to the CE separation and determination of various metal ions with enhanced selectivity and sensitivity relative to previously reported metal complexation CE techniques. Application to the analysis of complex sample matrices, containing high levels of acids and complexing agents, was demonstrated.

1. Introduction

High-performance capillary electrophoresis (CE) of metal ions after precolumn complexation is distinguished by a number of advantages in comparison with other CE methods. First, complete complexation before the separation largely eliminates interferences from complex sample matrices (*e.g.*, serum [1,2], pharmaceutical preparations [3], electroplating solutions [4] and ores [5]). Second, varying complex-forming conditions can additionally increase the selectivity of the metal analysis. Third, it is possible to separate metal ions that possess a slow rate of complexation or that are incompatible with the carrier electrolytes commonly used in CE [4,5]. When using light-absorbing chelating reagents [1,2,6,7], the sensitivity of direct spectrophotometric detection of metal ions is comparable to or better than that of CE with indirect UV detection. Further, there are no special restrictions on the types of ions that can be used in the electrophoretic buffer (a large difference in mobility of the carrier electrolyte ion and the analyte ion leads to excessive peak tailing/fronting in other CE methods).

Nevertheless, the precolumn metal complex-

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ation technique still lags behind other CE methods in some analytical characteristics, most conspicuously in the number of cations that can be simultaneously determined. In our opinion, further progress in this respect could depend on the application of micellar buffer systems. The separation principle of micellar CE [or micellar electrokinetic chromatography (MEKC)] is based on two mechanisms, micellar solubilization and electrokinetic migration, and this provides a wider option in optimization and additional possibilities for the enhancement of the separation selectivity [8,9]. In addition, micellar CE is not limited to electrically charged solutes so that its applicability can be extended to neutral metal chelates, as illustrated by Saitoh *et al.* [10,11], who separated metal acetylacetonato complexes in micellar solutions of sodium dodecyl sulphate (SDS). A few MEKC separations of negatively charged metal chelates have been reported [12–14], but with a limited number of separated metals and long analysis times. In a recent paper [15], we attempted to improve the resolution for metal complexes of 8-hydroxyquinoline-5-sulphonic acid (HQS) using SDS as a charged surfactant, but were able to observe only a minor effect of the micellar partitioning on mobility differences (probably because of the comparatively low hydrophobicity of the solutes).

This paper presents results from a continuation of our investigations on the CE of metal complexes in micellar electrophoretic systems. We studied the utility of 4-(2-pyridylazo)resorcinol (PAR) and Arsenazo III as chelating reagents that form intensely coloured, highly stable chelates with a wide variety of metal ions. Attention was also given to a comparison of the resolving powers attainable in pure and micellar CE systems. By using the effective mobility as a migration parameter, the influence of micellar solubilization was established. Also discussed are the common features in the migration behaviour of the complexes. Conclusions about the separation mechanism are presented along with a discussion of the analytical potential of the method.

2. Experimental

2.1. Chemicals

4-(2-Pyridylazo)resorcinol (PAR) and Arsenazo III [disodium salt of 2,7-bis(2-arsonophenylazo)-1,8-dihydroxynapthalenedisulphonic acid] were purchased from Merck (Darmstadt, Germany) and Aldrich Chemie (Steinheim, Germany), respectively, and used as a $5 \cdot 10^{-3}$ *M* stock solution in 0.01 *M* sodium tetraborate. Standard solutions of metal ions were prepared from the nitrates, except for vanadium, zirconium, tin and uranium, which were ammonium metavanadate, zirconium oxychloride, tin dioxide and uranyl acetate, at a concentration $2 \cdot 10^{-3}$ *M* in 0.01 *M* HNO_3. Sodium dodecyl sulphate (SDS) from Serva (Heidelberg, Germany) was dissolved in the corresponding buffer. Buffer solutions were prepared from sodium tetraborate or by mixing sodium (or ammonium) monohydrogenphosphate and dihydrogenphosphate in appropriate ratios. The pH values indicated below were measured after addition of SDS. The carrier electrolytes also contained an appropriate amount of a chelating reagent (usually $1 \cdot 10^{-4}$ *M*). All chemicals were of analytical-reagent grade and all solutions were prepared using doubly distilled water.

Metal complexes were prepared by direct mixing of metal and reagent standard solutions before the injection, unless stated otherwise.

2.2. Apparatus and procedure

Analyses were performed on Waters (Milford, MA, USA) Quanta 4000 and Applied Biosystems (San Jose, CA, USA) Model 270A CE systems equipped with a positive high-voltage power supply and fused-silica capillaries of 75 μm I.D. Detection was carried out by on-column spectrophotometric measurements at specified wavelengths. Electropherograms were recorded and processed with a Hewlett-Packard Model 3359 data acquisition system. Samples were introduced into the capillary at the anodic side by hydrostatic injections from a height of 10 cm

(Quanta 4000) or by applying a vacuum at a pressure of 16.9 kPa (Model 270A) for a specified time. To ensure day-to-day reproducibility of migration times, especially in the experiments with surfactant-rich electrolyte concentrations, the capillary was washed with 0.01 *M* NaOH for 30 min before the work.

The electroosmotic flow (EOF) velocity (or migration time of the bulk eluent) was determined from the migration time of acetone added to a sample. The effective mobility, μ_{eff}, was calculated as the difference between the observed mobility, μ_{ob}, and electroosmotic mobility, μ_{eo}, and expressed as negative values because it is opposed to the latter. Capacity factors, k', were calculated according to $k' = (t - t_0)/t_0$, where t and t_0 are the migration time of a solute and neutral marker, respectively. Such calculations are not affected by uncertainties in the electrophoretic mobility of the micelles and the true ionic electrophoretic mobility of the complexes.

2.3. Sample preparation

An accurately weighed amount of a zirconium ceramic (85% ZrO_2, 10% Nb_2O_5, 5% Ta_2O_5) was melted with 3 g of NaF and 4.5 g of H_3BO_3 in a platinum crucible, heating at 1000°C for 30 min. The melt was treated with a requisite amount (*ca.* 60 ml) of concentrated H_2SO_4 and the mixture was heated at 120°C until the solid was completely decomposed (*ca.* 1 h). The solution was cooled and then diluted to 250 ml with 10% tartaric acid. A 1-ml portion of the resulting solution was used for injection after filtering this solution through a PTFE membrane syringe filter and mixing with an equal volume of Arsenazo III standard solution. The corresponding blank solutions were prepared similarly, but without the addition of ceramic.

The same procedure was used to prepare zirconium and tantalum standard solutions from the corresponding oxides, whereas niobium oxide was dissolved by melting with $K_2S_2O_7$ followed by treatment with H_2SO_4 and tartaric acid.

3. Results and discussion

3.1. Pyridylazoresorcinolates

Saitoh *et al.* [12] were the first to demonstrate the feasibility of resolving transition metal ions in form of PAR complexes using micellar CE. They reported a 30-min separation of cobalt (III), chromium(III), nickel(II) and iron(III) chelates in a silica capillary with a 20 m*M* SDS micellar buffer. Later, the same group obtained good efficiency and a short analysis time (within 6 min) for the separation of PAR and its complexes with Co(III), Fe(II), Ni(II) and V(V) in a CE system without a micellar phase [7]. Both CE techniques demonstrated separations of only a limited number of metal ions, especially in comparison with metal CE analysis based on partial in-capillary complexation [9]. Based on this, the aim of the present study was also to achieve an improved peak capacity for separations of metal–PAR complexes with no decrease in analysis times.

In the initial experiment, borate electrophoretic buffers were tested to evaluate the effect of different concentrations of SDS. The buffers were prepared with increasing amount of the surfactant in sodium tetraborate solution without further pH adjustments (the effect of SDS concentration on the pH was limited to 0.05 unit). As can be seen in Table 1, the results are essentially the same as those obtained previously for metal–HQS complexes [15]. The effective mobilities of PAR complexes and their relative migration velocities calculated from the differences in k' values are largely unaffected by the surfactant concentration. As the complexes exist as doubly charged species under the alkaline conditions employed (Fig. 1, $n = 2$; according to the acid dissociation constants [7,12] both 1-hydroxy groups of PAR ligands are fully deprotonated at pH 9.0), strong repulsion between anionic solutes on the one hand and negatively charged head groups of micelles on the other probably suppresses any partitioning processes. Therefore, the increased migration times observed in the presence of micelles are solely a

Table 1
Effective mobilities and capacity factors of metal–PAR complexes at different concentrations of SDS in the borate electrophoretic buffer

Complex	SDS (mmol/l)					
	0		50		150	
	$\mu_{eff} \times 10^5$ (cm^2/V·s)	k'	$\mu_{eff} \times 10^5$ (cm^2/V·s)	k'	$\mu_{eff} \times 10^5$ (cm^2/V·s)	k'
Cu(II)	27.1	0.60	26.7	0.76	27.0	0.81
Fe(III)	27.9	0.61	27.5	0.72	27.9	0.83
Ni(II)	27.8	0.62	27.6	0.73	26.7	0.78
Zn(II)	28.4	0.63	28.9	0.75	–	–
PAR	23.0	0.45	24.8	0.58	26.4	0.76

Capillary, 35/42 cm × 75 μm I.D.; pH, 9.0; voltage, 15 kV.

result of the decreased EOF velocity, changing from $73.6 \cdot 10^{-5}$ cm^2/V·s under normal CE conditions to $63.6 \cdot 10^{-5}$ cm^2/V·s and then $60.8 \cdot 10^{-5}$ cm^2/V·s at 50 and 150 m*M* SDS, respectively. Only the free chelating reagent, which is singly charged in this pH range, showed a lower effective mobility (along with a higher retention relative to the complexes) with increasing SDS concentration. This behaviour may have been related to the effect of micellar solubilization.

As the resolution of closely related complexes was not improved by changing the surfactant concentration alone, it was decided to continue to investigate the micellar CE behaviour with phosphate carrier electrolytes. The electropherograms shown in Fig. 2 illustrate the influence of compositional buffer changes on the resolution of a test mixture of five complexes. For a phosphate buffer at pH 8.0, the migration time remains almost unchanged at constant micellized SDS concentration, whereas the resolution was slightly improved (*cf.*, electropherograms a and b). However, the choice of metal counter ion in the carrier electrolyte influences the separation selectivity more drastically. When disodium hydrogenphosphate was replaced with diammonium hydrogenphosphate, which resulted in the replacement of about 28% of the

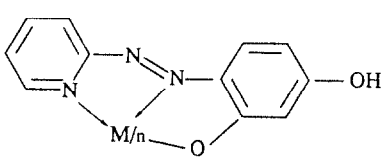

Fig. 1. Structure of metal–PAR complexes.

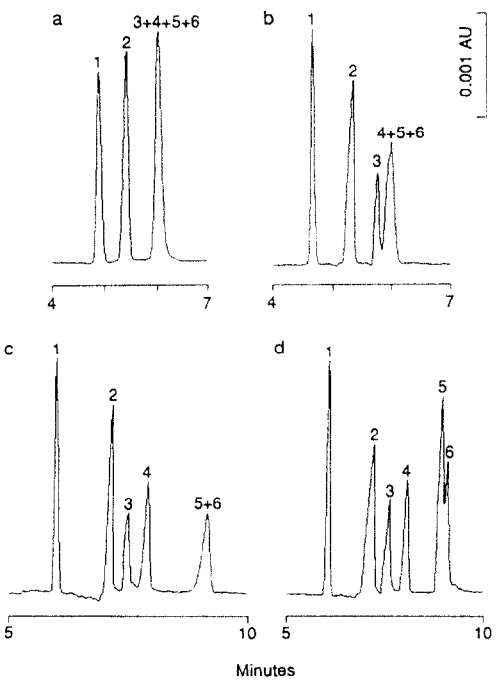

Fig. 2. Electropherograms of metal–PAR complexes with different micellar carrier electrolytes: (a) $Na_2B_4O_7$; (b) Na_2HPO_4–NaH_2PO_4; (c) $(NH_4)_2HPO_4$–NaH_2PO_4; (d) $(NH_4)_2HPO_4$–$NH_4H_2PO_4$. All buffers were 10 m*M* and contained 50 m*M* SDS and $1 \cdot 10^{-4}$ *M* PAR. Capillary, 35/42 cm × 75 μm I.D.; voltage, 15 kV; injection, 10 s (hydrostatic); detection, 254 nm. Peaks: 1 = Co(III); 2 = PAR; 3 = Cu(II); 4 = Ni(II); 5 = Fe(III); 6 = Zn(II).

Table 2
Effect of metal counter ion of the phosphate electrophoretic buffer on effective mobilities of metal–PAR complexes

Complex	$\mu_{eff} \times 10^5$ ($cm^2/V \cdot s$)		
	Na_2HPO_4–NaH_2PO_4	$(NH_4)_2HPO_4$–NaH_2PO_4	$(NH_4)_2HPO_4$–$NH_4H_2PO_4$
Co(III)	21.7	22.9	23.6
Cu(II)	28.4	30.7	30.7
Fe(III)	29.6	35.9	35.1
Ni(II)	29.6	32.2	32.2
PAR	26.2	29.4	29.3

Capillary, 35/42 cm × 75 μm I.D.; SDS, 50 mmol/l; pH, 8.0; voltage, 15 kV.

sodium ions in the micellar buffer, the effective mobilities were decreased, as can be seen from the results of Table 2. Referring to Fig. 2, this leads to complete resolution of copper, nickel and iron (or zinc) complexes; however, the latter two still co-migrates. In a buffer containing both components as ammonium salts, the peaks of iron and zinc were partially resolved, although the μ_{eff} values remained virtually unchanged (see Table 2).

As expected, these data can be well explained in terms of ion-pair formation between the solute and the cationic component of the electrophoretic buffer. Ammonium ion acting as a stronger ion-pairing cation than sodium ion decreases the negative charge of the complexes through ion association and thereby diminishes the electrostatic repulsion, facilitating the incorporation of paired complexes by the micelle. Nevertheless, the elution order for the complexes is not different from that in a pure CE migration system. This seems to indicate that the electrophoresis predominates over the interaction with the micelle in the migration behaviour even with SDS–ammonium salts present in buffer solutions. Phosphate buffers of lower pH were found to be less suitable for separation as the migration times appeared to be longer (owing to the decreased EOF) without any significant change in selectivity. Further experiments were therefore conducted with the buffer consisting of $(NH_4)_2HPO_4$–$NH_4H_2PO_4$ (pH 8.0).

Based on the aforementioned results, we decided to study further the micellar effect on the optimum separation of PAR complexes. Increasing the surfactant concentration in an optimized buffer electrolyte system produced a gradual decrease in the migration velocities of solutes. In this experiment, the concentration of SDS was increased in several steps up to 150 m*M*. The decrease in migration velocities was considered to be a result of cooperative effects of changes in the phase ratio and electroosmotic mobility (due to changes in viscosity and ionic strength). Together with longer run times, we were able to observe that the resolution was enhanced. Therefore, an SDS concentration of 75 m*M* in the buffer, providing the separation of most of the complexes under consideration within 10 min, was concluded to be optimum.

Fig. 3 displays an electropherogram showing the optimized separation of a nine-component metal ion mixture. Metals that form PAR complexes less stable than that of cadmium (manganese, alkaline earths, etc.) could not be detected under the experimental conditions used. The vanadium (V)–PAR complex migrated very close to the copper chelate, whereas La(III), Zr(IV), Sn(IV) and U(VI) complexes exhibited

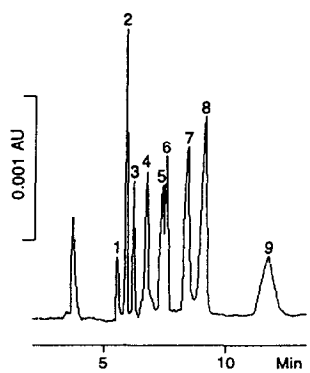

Fig. 3. Micellar CE separation of metal chelates of PAR. Capillary, 42/50 cm × 75 mm I.D.; carrier electrolyte, 10 m*M* ammonium phosphate buffer containing 75 m*M* SDS and $1 \cdot 10^{-4}$ *M* PAR (pH 8.0); voltage, 15 kV; injection, 30 s (hydrostatic); detection, 254 nm. Metals (mol/l): 1 = Cr(III) ($2.4 \cdot 10^{-4}$); 2 = Co(II) ($6 \cdot 10^{-5}$); 3 = Cu(II) ($8 \cdot 10^{-5}$); 4 = Pb(II) ($8 \cdot 10^{-5}$); 5 = Ni(II) ($8 \cdot 10^{-5}$); 6 = Fe(II) ($8 \cdot 10^{-5}$); 7 = Zn(II) ($1.6 \cdot 10^{-4}$); 8 = Fe(III) ($8 \cdot 10^{-5}$); 9 = Cd(II) ($2.4 \cdot 10^{-4}$). The first-migrating peak belongs to acetone.

broad and asymmetric peaks with smaller peak heights. The formation of the chromium(III) complex requires the use of triethanolamine as an auxilary ligand for acceleration of complexation; we followed the procedure described in ref. 16 after a minor alteration of the conditions (high contents of triethanolamine affect the migration times). It should be noted that by varying the reagent-to-metal ratio in the injected sample solution one can attain a decrease in the PAR peak intensity until its complete disappearance. Of practical importance also is the possibility of differentiating between different oxidation states of iron.

Further optimization of analytical performance of the PAR chelating system was directed towards detectability enhancement. CE systems from two different manufacturers were utilized for these experiments (see Experimental). When the detection of complexes is accomplished in the visible spectral range, a general increase in sensitivity will be expected. Limits of detection, defined as three times the baseline noise, are summarized in Table 3. Injections of the same duration correspond to *ca.* five times higher injected volumes with the Model 270A (with due regard to differences in capillary length). Therefore, for the purposes of comparison, the corresponding detection limits were evaluated in an 8-nl injection volume. As can be seen, increased peak intensities and a smaller background signal when the detection wavelength was fixed at 500 nm resulted in substantially better performance than UV detection performed on the Quanta 4000. An illustrative electropherogram showing a peak near the limit of detection for the cobalt–PAR chelate is presented in Fig. 4.

Table 3
Detection limits (mol/l) of metal ions as PAR complexes

Metal ion	Detection wavelength (nm)	
	254[a]	500[b]
Co(II)	$8 \cdot 10^{-7}$	$1 \cdot 10^{-7}$
Cu(II)	$2 \cdot 10^{-6}$	$6 \cdot 10^{-7}$
Fe(III)	$4 \cdot 10^{-6}$	$9 \cdot 10^{-7}$
Ni(II)	$3 \cdot 10^{-6}$	$1 \cdot 10^{-6}$
Zn(II)	$2.4 \cdot 10^{-5}$	$8 \cdot 10^{-7}$

[a] Quanta 4000; injection time, 5 s (*ca.* 8 nl).
[b] Model 270A; evaluated in an 8-nl injection volume.

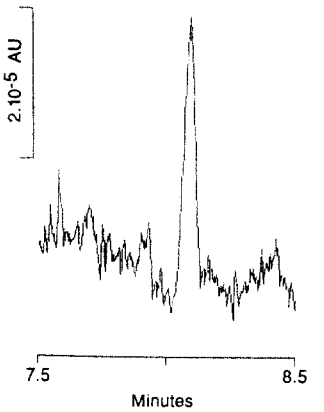

Fig. 4. Detectability of cobalt–PAR complex ($1 \cdot 10^{-7}$ *M*) near the detection limit. Capillary, 43/63 cm × 75 μm I.D.; voltage, 20 kV; injection 5 s (vacuum); detection, 500 nm. Carrier electrolyte as in Fig. 3.

3.2. Complexes of Arsenazo III

Initial studies were carried out with the borate buffer systems shown in Table 4. Also given in Table 4 are the migration characteristics of various metal chelates and the reagent. Their comparison with the corresponding data for PAR complexes (see Table 1) indicates that metal–Arsenazo III complexes exhibited far larger retentions under both normal and micellar CE conditions. This is thought to be a result of their higher electrophoretic mobility. This observation is in accord with the higher charge of complexes containing several ionizable groups that do not participate in complexation (Fig. 5); according to data on the acid ionization of Arsenazo III [17], at pH 9 both sulphonic and arsonic groups are ionized (one completely and the other partially). The capability of this reagent to form complexes with a 1:1 and 2:1 metal-to-ligand stoichiometry also favours a higher electrophoretic mobility. Nevertheless, we always observed the migration of Arsenazo III complexes towards the cathode (the detection side). Correspondingly, the electroosmotic velocity must have been always high-

Table 4
Effective mobilities and capacity factors of metal–Arsenazo III complexes in different borate carrier electrolytes

Complex	Borate buffer		Borate buffer + $1 \cdot 10^{-4}$ *M* Arsenazo III		Borate buffer + $1 \cdot 10^{-4}$ *M* Arsenazo III + 50 m*M* SDS		Borate buffer + $1 \cdot 10^{-4}$ *M* Arsenazo III + 100 m*M* SDS	
	$\mu_{eff} \times 10^5$ ($cm^2/V \cdot s$)	k'	$\mu_{eff} \times 10^5$ ($cm^2/V \cdot s$)	k'	$\mu_{eff} \times 10^5$ ($cm^2/V \cdot s$)	k'	$\mu_{eff} \times 10^5$ ($cm^2/V \cdot s$)	k'
Cu(II)	43.1	1.59	44.7	1.45	42.2	1.63	41.4	1.78
Fe(III)	44.8	1.62	46.1	1.52	44.6	1.83	43.1	1.95
La(III)	41.2	1.29	41.0	1.15	42.2	1.55	39.7	1.48
Pb(II)	–	–	–	–	43.0	1.58	40.6	1.64
Arsenazo III	45.7	1.68	46.8	1.66	45.3	1.88	43.9	2.02

Capillary, 42/50 cm × 75 μm I.D.; pH, 9.0; voltage, 15 kV.

er than the electrophoretic velocity of any of the solutes employed.

The second distinctive feature of the discussed chelating system is the formation of metal complexes under more acidic conditions. As shown below, this permits the applicability of metal complexation CE to be extended to highly acidic samples (*e.g.*, after decomposition with mineral acids). In fact, the optimum complexation required a slight change in the procedure, that is, addition of nitric acid to the metal solution in a 1:1 ratio before mixing with the reagent solution.

The micellar CE behaviour of Arsenazo III complexes with respect to the surfactant concentration was studied also for ammonium phosphate electrolytes. The addition of SDS gave rise to an enhanced retention but this effect was evidently caused by the corresponding changes in the electroosmotic mobility. Typical results in terms of μ_{eff} *versus* surfactant concentration are depicted in Fig. 6. It can be seen from these profiles that as the SDS concentration was varied between 25 and 100 m*M*, the effective mobilities increased. This phenomenon is believed to be attributable to changes in the true ionic mobility of the analytes with the parameter studied. As would be expected from the highly acidic nature of the ligand's sulphonic and arsonic groups, the effective mobilities are insensitive to pH in the range more suitable for counter-electroosmotic migration [9] (we particularly investigated the pH range 6.5–8 in an attempt to improve the resolution). Therefore, as with HQS complexes [15], the dependence of charge on pH could not be exploited to obtain better micellar CE separations.

Taking into account the higher charge of Arsenazo III complexes, it is unlikely that they are solubilized by the anionic SDS micelle owing to electrostatic repulsion. In addition, the small dimensions make micelles less suitable for the solubilization of large aggregates such as these complexes. Consequently, unlike PAR complexes, they migrated due to the electrophoresis of

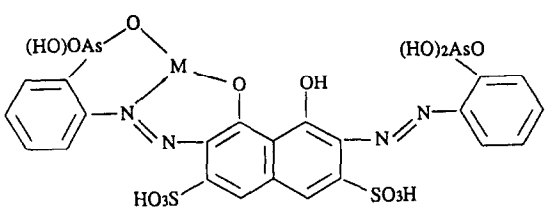

Fig. 5. Molecular structure of metal–Arsenazo III complexes.

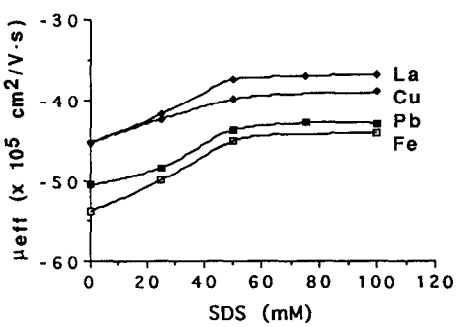

Fig. 6. Effective mobility of metal–Arsenazo III complexes as a function of surfactant concentration. Carrier electrolyte, 10 m*M* $(NH_4)_2HPO_4$–$NH_4H_2PO_4$ containing $1 \cdot 10^{-4}$ *M* Arsenazo III (pH 8.0). Other conditions as in Table 4.

the solute itself without any interaction with the micellar phase. When using micellar buffer solutions, the separations become longer and less efficient without any observable increase in selectivity. Fig. 7 distinctly shows the superiority of the resolving power of CE with no surfactant in the electrophoretic buffer. Also, the presence of SDS was found to affect adversely the detectability (note also the appearance of an additional negative excursion from the baseline).

On the basis of the above results, non-micellar CE with a phosphate buffer of pH 7.0 was chosen as the optimum migrating system. We also investigated CE separations of other metals not shown in Fig. 7 under same conditions. Rare earth complexes co-migrated with that of lanthanum, whereas the zirconium complex had a mobility close to that of the iron chelate; in the presence of tartaric acid both niobium and tantalum formed mixed-ligand complexes [17] that probably led to large irregularities in their retention behaviour (see below); nickel, chromium and molybdenium complexes produced badly asymmetric peaks; no migration of zinc, manganese, vanadium, bismuth and alkaline earth metal complexes was observed.

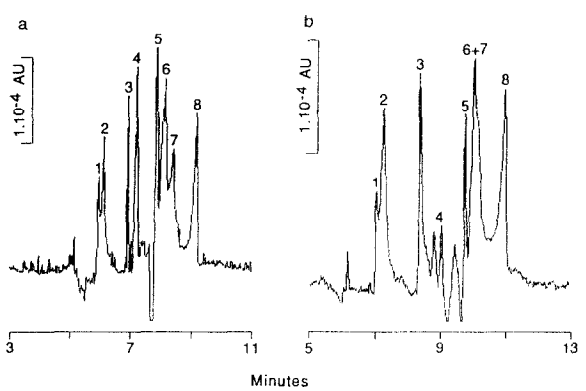

Fig. 7. Comparison between (a) pure CE and (b) micellar CE performance for metal–Arsenazo III complexes. Capillary, 42/50 cm × 75 μm I.D.; carrier electrolyte, (a) 10 m*M* $(NH_4)_2HPO_4$–$NH_4H_2PO_4$ containing $1 \cdot 10^{-4}$ *M* arsenazo III (pH 8.0); (b) same as (a) + 50 m*M* SDS; voltage, 20 kV; injection, 2 s (hydrostatic); detection, 254 nm. Peaks: 1 = Ce(III); 2 = La(III); 3 = U(VI); 4 = Cu(II); 5 = Arsenazo III; 6 = Pb(II); 7 = Co(II); 8 = Fe(III). Concentration of all metals $1.5 \cdot 10^{-4}$ *M*, except La ($3 \cdot 10^{-4}$ *M*) and U ($7.5 \cdot 10^{-5}$ *M*).

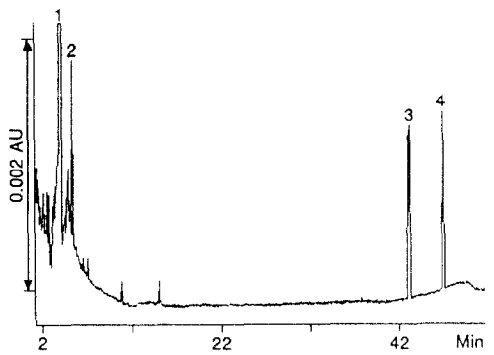

Fig. 8. CE analysis of a zirconium ceramic. Voltage, 28 kV; injection, 15 s. Other conditions as in Fig. 7a. Peaks: 1 = Arsenazo III; 2 = zirconium (196 ppm); 3 = niobium (23 ppm); 4 = tantalum (23.5 ppm).

Evaluation of the applicability of the Arsenazo III chelating system to real samples was performed with the analysis of zirconium ceramics containing niobium and tantalum as alloying additives. The baseline-resolved separation of all metallic constituents of the sample was achieved under the optimum separation conditions outlined (Fig. 8). Owing to the large differences in migration times, zirconium as a main component did not interfere with the detection of niobium and tantalum. For practioners of CE, it is also important to note that the only treatment of the analysed solution consisted in dilution and filtration (for additional details, see Experimental).

4. Conclusions

It has been shown that micellar electrophoretic systems can be applied to the CE separation of negatively charged metal complexes provided that these complexes possess a hydrophobic nature so as to be solubilized by anionic SDS micelles. With PAR complexes, both the electrophoretic mobility and micellar partitioning contribute to their separation; the latter seemingly has a smaller effect. The cationic component of the carrier electrolyte (*e.g.*, ammonium) can act as an ion-pairing counter ion and help to overcome electrostatic repulsion between anionic solutes and negatively charged head groups of the micelle. This alters the relative contribution

of partitioning processes and leads to an improvement in resolution.

As demonstrated above, it is more difficult to manipulate the retention behaviour of highly ionized solutes, *e.g.*, metal–Arsenazo III complexes. The limited capacity of micellar CE with respect to these chelates is also consistent with the larger size of the molecules making solubilization more difficult. In consequence, their separation is not influenced by variations in the SDS concentration and is based exclusively on differences in electrophoretic mobility. The same observation is valid for other metal complexes with "hydrophilic" ionizable groups, such as 5-sulphohydroxyquinolinates [15] and N-methyl-N-2-sulphoethyldithiocarbamates, currently under investigation in our laboratory. On the other hand, metal–Arsenazo III complexes demonstrate the impressive selectivity in the non-micellar CE mode that provides good separations for a variety of metal ions.

In conclusion, the chelating systems described here show promise regarding the expansion of the analytical potential of metal complexation CE toward the achievement of multi-element separations with good detectability. Possibilities of further improvements still exist and will be explored in future work. Immunity of CE based on precolumn complexation to complex sample matrices, which are currently impossible to analyse by using present CE methodology, is especially attractive. Therefore, this method will well complement traditional approaches to the separation and determination of metal ions by CE.

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6. References

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