Control of separation selectivity and electroosmotic flow in nonaqueous capillary electrophoretic separations of alkali and alkaline earth metal ions

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Abstract

Factors affecting the separation selectivity and electroosmotic flow (EOF) for the separation of alkali, alkaline earth cations, and ammonium ion in nonaqueous systems were evaluated. The nature of electrolyte anion (chloride, perchlorate, and acetate) and solvent (methanol–acetonitrile mixtures) had important effects on the EOF in acidic conditions. Evidence was observed for ion adsorption (protons and anions) on the silica surface and for ion-interactions in the electrolyte; both effects could be used to control the direction and magnitude of the EOF. Relative to aqueous systems, unique separation selectivity was achieved for alkali and alkaline earth cations; ammonium and alkali cations were resolved from alkaline earth cations and potassium and ammonium ions were well separated. Calibration of all the cations gave linear curves in the range of $5\times10^{-4}-5\times10^{-5}$ mol/l; detection limits (indirect with imidazole) were in the range of $7\times10^{-6}-2\times10^{-5}$ mol/l. To evaluate this system, the separation of metal ions was examined for a brine solution and an aqueous soil extract sample.

Keywords: Electroosmotic flow; Separation selectivity; Alkaline earth metals; Alkali metals

1. Introduction

Capillary electrophoresis (CE) has become a powerful separation technique in recent years because of its speed, resolving power, minimal reagent consumption and the availability of several different separation modes. This technique has been extensively examined for potential analytical application to many different analyte types. One of these areas is the separation of small ions such as inorganic cations, anions and amino acids [1–3]. Although ion-chromatography has been successfully applied to the separation and determination of a variety of

anions and cations [4,5], the attractive features of CE have led many people to examine the electrophoretic separation of alkali and alkaline earth metal ions in different aqueous electrolytes [6–14]. However, the separation of some of these metal ions is still considered difficult, particularly for potassium and ammonium ions. Separations of sodium/magnesium and calcium/strontium are also difficult when the concentration of one is considerably higher than the other [8,13], even when complexing agents are used to improve separation selectivity and resolution [6–9]. Consequently other approaches are needed.

Recently it has been shown that the use of "pure" nonaqueous systems may offer potential for adjustment of relative migration rates via changes in

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solvation and ion-interaction [15,16]; evidence for such analyte–electrolyte interactions has been reported for separation of inorganic anions [15] and anionic surfactants [16]. In addition, a limited number of other studies have also examined some aspects of the use of nonaqueous systems for CE [17–19]. In this study the separation of alkali and alkaline earth cations and ammonium ion was examined in methanol and methanol–acetonitrile mixtures. Since little is known about the behavior of electroosmotic flow (EOF) in pure nonaqueous systems, this feature was also examined. The cations were detected by indirect UV absorbance at 214 nm, and different indirect UV reagents were evaluated for separation and detection of these metal ions. Analytical performance of the system was examined and applied to the separation of some alkali and alkali metal ions in a brine solution and an aqueous soil extract sample.

2. Experimental

2.1. Instrumentation

A Quanta 4000 (Waters Chromatography, Milford, MA, USA) CE unit was used for UV detection (214 nm). Capillaries were 75 μm I.D. and 370 μm O.D. (Polymicro Technology, Phoenix, AZ, USA), with an end-to-end length of 50 cm and injection-to-detection length of 43 cm. Samples were injected hydrostatically by elevation of the sample vials to 10 cm for 5 s unless specified otherwise. Applied voltage for both separation and electroosmotic measurements was 20 kV (either positive or negative). The tip of the solvent peak or benzyl alcohol was used as a neutral marker for the EOF measurements; cathodic EOF (towards the negative electrode) was considered to be positive, while anodic EOF (towards the positive electrode) was considered to be negative. Capillaries were washed with electrolyte for 1 min between runs by application of vacuum (15 mm Hg).

2.2. Chemicals

All sample solutions were prepared from deionized water that was double distilled (Corning, Mega-Pure System, MP-6A and D2, NY, USA). Tetraethylammonium hydroxide (TEAOH) (25% w/v in methanol) was purchased from Sigma (Sigma, St. Louis, MO, USA). Tributylbenzylammonium chloride (TBBAC) and imidazole were purchased from Aldrich (Aldrich, Milwaukee, WI, USA). $HClO_4$, HCl, methanol and acetonitrile were purchased from BDH.

2.3. Procedures

Stock solutions of (0.01 mol/l) ammonium, alkali and alkaline earth metal ions (all in nitrate form), were prepared in deionized water, and samples were diluted to the desired concentration with water before the introduction of sample. The waste brine solution, obtained from a potash fertilizer mining operation, contained 280 g/l NaCl and 130 g/l KCl, and was diluted a 1000-fold in water prior to injection. The soil sample was obtained by an aqueous extraction (135 ml water and 250 g soil) and filtered prior to injection. All electrolytes were prepared daily; the final water content of electrolytes was ~0.1% v/v. Separation electrolyte was changed every 4 h. All electrolytes and samples were filtered through a 0.2-μm Nylon-66 membrane syringe filter (Cole-Parmer, Chicago, IL, USA) immediately prior to use. New capillaries were conditioned by washing with methanol for 1 h, followed by another 2 h with the separation electrolyte by the use of 10 cm height differential; for long-term storage, capillaries were flushed with methanol. All glassware was rinsed with a chromic/sulfuric acid solution followed by water and acetone and then dried in an oven. The number of theoretical plates was calculated from, $N = 5.54(t_R/w_{0.5})^2$, where t_R is the migration time of analyte, and $w_{0.5}$ is the peak width at half peak height. Electroosmotic mobilities were calculated from $\mu_{eo} = Ll/(t_{eo}V)$, where μ_{eo} is electroosmotic mobility, t_{eo} is the migration time for the neutral marker in s, V is the separation voltage in volts, L is the capillary length and l is injection-to-detection length in cm. The electrophoretic mobilities (μ_{ep}) of ions were calculated from, $\mu_{ep} = \mu_{eo} + Ll/(t_{ep}V)$ where t_{ep} is the migration time for analyte. Detection limits were defined as the concentration required to give peak heights of twice peak-to-peak noise. The linearity of calibration curves was evaluated from plots of sensitivity vs. concentration [20]. The sensitivity, S, was obtained from, $S = (I - b)/C$, where I

and C are the response and concentration, respectively, and b is the Y-axis intercept obtained from the analysis of least-squares regression using the original response–concentration data [20].

3. Results and discussion

3.1. Electroosmotic flow

Properties of a solvent are important for understanding and control of EOF and μ_{ep} of ions; these include dielectric constant (ϵ), viscosity (η), donor number and solvating ability [21–23]. The solvation of ions can influence ion-interaction; the term of ion-interaction is used to represent any ion-association (Brønsted acid association), ion-pairing, or ion-cluster formation that may occur in nonaqueous systems. Solvation depends on the physico-chemical properties of the solvent, and a general classification often used is protic/aprotic. In a protic solvent, hydrogen bonding is strongest for the smallest anions and those with localized charge such as chloride and acetate. It becomes progressively weaker as the size of the anions increases. For example, in methanol (protic solvent), the solvation of chloride and acetate is favored due to formation of hydrogen bonds. However, perchlorate ion, which is larger than chloride and acetate, is more polarizable and is preferentially solvated by acetonitrile (aprotic solvent) by a combination of dispersion and ion–dipole interactions [24]. For a protic solvent, such as methanol, changes in ion association for a series of tetraethylammonium salts follow trends similar to that found in water [24], but in an aprotic solvent such as acetonitrile, significantly different trends are expected. More detailed description of the behavior of salts in nonaqueous solvents can be found elsewhere [21–25].

Control and characterization of EOF is important in the evaluation of reproducibility and for peak identification. Ion mobility and EOF in some nonaqueous media have been reported recently [15] and appreciable EOF was observed in methanol and dimethylformamide (50 to 70% of that for aqueous systems). Electrophoretic mobilities of analytes ions, μ_{ep}, were two to three times higher than electroosmotic mobility [15] and the magnitude of μ_{ep} and

μ_{eo} depended on the electrolyte system. In methanol and dimethylformamide the direction of EOF is cathodic in basic conditions [15], but no studies have been reported for nonaqueous acidic electrolytes. Since it was preferable to separate alkali and alkaline earth cations in acidic conditions to prevent possible hydrolysis of alkaline earth cations with the small amounts of water (0.1% v/v) in the nonaqueous solvents, the EOF behavior for acidic methanol and methanol–acetonitrile mixtures was examined. Fig. 1 shows electroosmotic mobility patterns observed as a function of solvent composition (mixtures of a protic and aprotic solvent) in three different acidic electrolytes: in curve A the electrolyte anion is chloride (0.01 mol/l tetraethylammonium chloride (TEAC) and 0.01 mol/l HCl in methanol); in curve B the electrolyte anion is ClO_4^- (0.01 mol/l tetraethylammonium perchlorate (TEAP) and 0.01 mol/l $HClO_4$ in methanol); and in curve C the electrolyte anion is acetate (0.01 mol/l tetraethylammonium acetate (TEAA) and 0.01 mol/l acetic acid in methanol). With the chloride electrolyte (Fig. 1, curve A), the observed anodic EOF (towards positive electrode)
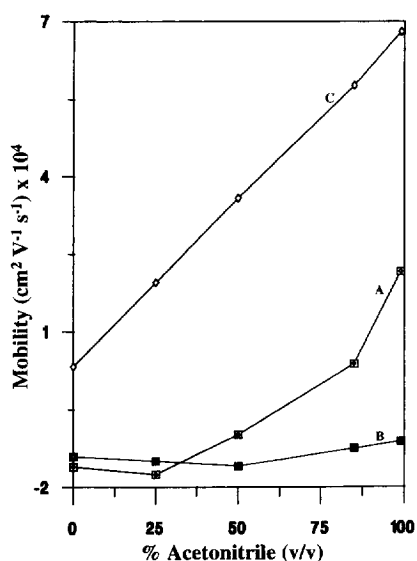

Fig. 1. Effect of the addition of acetonitrile to methanol electrolytes on electroosmotic flow. Experimental conditions: electrolyte, (A) 0.01 mol/l TEAC and 0.01 mol/l HCl (B) 0.01 mol/l TEAP and 0.01 mol/l $HClO_4$ (C) 0.01 mol/l TEAA and 0.01 mol/l acetic acid in methanol; 50 cm capillary (75 μm I.D.) with injection-to-detection length of 43 cm; separation voltage, 20 kV, either positive or negative; indirect detection at 214 nm.

decreased with concentration of acetonitrile and, after passing through a minimum, it increased until eventually at ~75% v/v acetonitrile the direction of the EOF changed to cathodic. With the ClO_4^- electrolyte (Fig. 1, curve B), the EOF showed the same overall pattern as chloride, but the EOF was always anodic. With the acetate/acetic acid electrolyte, however, the EOF was always cathodic and increased with the concentration of acetonitrile (Fig. 1, curve C).

The different patterns shown in Fig. 1 appear to be related to a combination of effects arising from adsorption of cation and anions onto the capillary wall and from differences in ion-interaction. The anodic EOF for HCl and $HClO_4$ in methanol implies the presence of a net positive charge at the surface of the capillary. This positive charge could be attributed to the adsorption of tetraethylammonium ion (TEA^+) and/or solvated protons (from excess acid) onto the capillary wall. Under acidic conditions, any negative charge on the surface of silica from dissociation of silanols (or adsorption of anions) is low, and adsorption of small amounts of any cation would result in a net positive charge. Adsorption of protons on silica surfaces has been reported in aqueous media at low pH [26], and reversal of EOF was reported for the addition of Mg^{2+} to a borate buffer (pH 8) [27]. Thus the anodic EOF for HCl and $HClO_4$ electrolytes can probably be attributed to the adsorption of solvated protons. This conclusion is supported by the anodic EOF values observed for 0.01 mol/l HCl in methanol ($\mu_{eo} = -3.644 \times 10^{-4}$ cm^2 V^{-1} s^{-1}) and for 0.01 mol/l $HClO_4$ in methanol ($\mu_{eo} = -1.125 \times 10^{-4}$ cm^2 V^{-1} s^{-1}). The EOF rates in 0.01 mol/l HCl and 0.01 mol/l $HClO_4$ are faster than those for the corresponding electrolytes in Fig. 1 (curves A and B), most likely as a result of a combination of smaller ionic strength (higher zeta potential) and reduced anion adsorption. While the adsorption of TEA^+ could also be a factor, this is most likely not significant for these studies because the EOF for the TEAA/acetic acid electrolyte was always cathodic. In addition, when Na^+ was used in place of TEA^+, similar EOF mobilities and trends were observed as a function of acetonitrile concentration.

To explain the patterns observed in Fig. 1 as function of acetonitrile concentration, it is necessary to postulate a combination of anion adsorption and ion-interaction effects. Although some of the trends

in EOF in Fig. 1, such as the small changes in EOF for lower acetonitrile concentrations might be attributed to changes in the ratio of dielectric constant to viscosity (ϵ/η) [28] as a function of acetonitrile content, this is not sufficient for explanation of the patterns seen at larger acetonitrile concentrations. If cation adsorption is significant (HCl and $HClO_4$ cases), increases in acid association constants with acetonitrile concentration will result in reduced cation adsorption and thus smaller EOF values. However, increased acid association can not explain the eventual change from anodic to cathodic EOF for HCl, nor the significant increase of EOF for acetate. These patterns can be explained if anions are also adsorbed onto the silica surface. Solvation of acetate and chloride should decrease relative to perchlorate upon the addition of acetonitrile (see above discussion on solvation of these ions) and this should increase any tendency for their adsorption onto silica surfaces. Thus, combined shifts in the equilibria for cation and anion adsorption, and for acid-association could explain the main features of the patterns seen in Fig. 1. The failure of EOF to become cathodic for the perchlorate electrolyte (curve B) at the higher acetonitrile concentration may be a result of more extensive solvation of perchlorate, which would reduce both ion-interaction and anion adsorption relative to chloride ion.

The importance of ion-interaction is also illustrated by results observed for current in the capillary as a function of acetonitrile concentration. Fig. 2 shows that currents in acetic acid electrolytes (curve C) were much lower than for HCl (curve A) and $HClO_4$ (curve B) electrolytes, because acetic acid is more associated. The separation current for both HCl and $HClO_4$ increased at lower concentrations of acetonitrile and, after passing through a maximum (which could be partially due to the change of ϵ/η in mixed methanol–acetonitrile), decreased at the higher concentrations of acetonitrile; this decrease was greater for HCl (see Fig. 2, curves A and B). The decrease in current for curves A and B at higher acetonitrile concentrations is likely a result of acid association. This conclusion is supported by results in curve D, Fig. 2, which shows a large decrease in separation current for an electrolyte containing only 0.01 mol/l HCl (equal to concentration of HCl in the electrolyte for curve A) as a function of concentration of acetonitrile; the current for 0.01 mol/l HCl
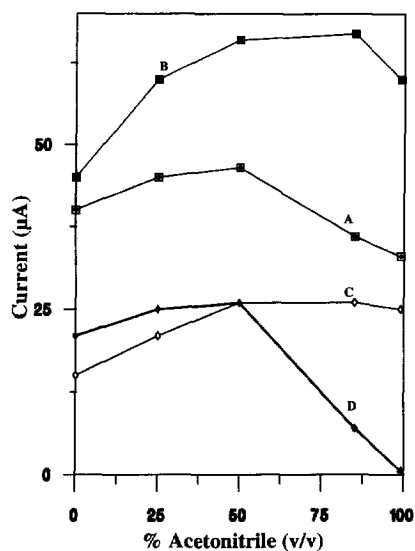
Fig. 2. Effect of the addition of acetonitrile to methanol electrolytes on the separation current. Experimental conditions: electrolyte, (A) 0.01 mol/l TEAC and 0.01 mol/l HCl (B) 0.01 mol/l TEAP and 0.01 mol/l $HClO_4$ (C) 0.01 mol/l TEAA and 0.01 mol/l acetic acid in methanol; (D) 0.01 mol/l HCl in methanol; other conditions as for Fig. 1.
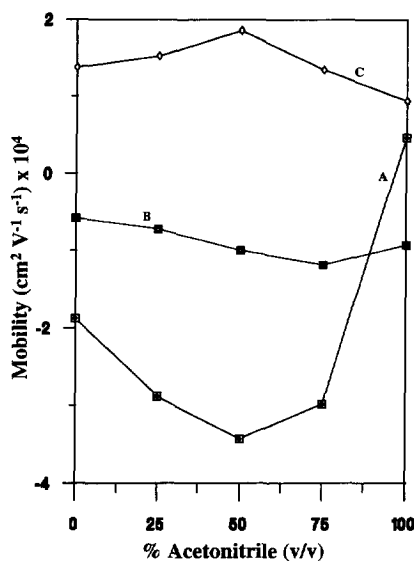

Fig. 3. Effect of the addition of acetonitrile to methanol on electroosmotic flow. Experimental conditions: electrolyte, 0.02 mol/l imidazole and 0.03 mol/l acid; (A) HCl (B) $HClO_4$ (C) acetic acid. Other conditions as for Fig. 1.

decreased to almost zero in pure acetonitrile. Thus the results in Fig. 2 suggest that ion-interaction between TEA^+ and acetate is not extensive and that $HClO_4$ is not associated as much as HCl in acetonitrile which is consistent with the literature pK_a values in acetonitrile (8.9 for HCl and <1 for $HClO_4$) [25,29].

Since the separation and detection of alkali and alkaline earth cations was studied in the presence of 0.02 mol/l imidazole (for indirect detection), the electroosmotic behavior of this electrolyte was also studied in the presence of excess hydrochloric, perchloric and acetic acids in methanol and methanol–acetonitrile mixtures. The EOF results in Fig. 3 show trends similar to those in Fig. 1 for TEA^+ electrolytes (Fig. 1), but EOF was generally faster in pure methanol electrolytes with HCl and acetic acid, possibly due to increased cation adsorption or increased ion-interaction. Significantly different trends were observed for the acetic acid imidazole electrolyte as a function of acetonitrile concentration. With this electrolyte (see Fig. 3) decreases in EOF were observed above 50% acetonitrile (compare curve C, Fig. 1). In addition, total current as a function of acetonitrile concentration for the imida-

zole/acetic acid system was two to eight times lower than that observed for the TEAA/acetic acid electrolytes shown in Fig. 2. Thus, it appears that there may be stronger ion-interaction in imidazole acetate electrolytes.

The above results show that the magnitude of EOF in these acidic nonaqueous systems is determined by a combination of anion adsorption, cation adsorption and ion-interaction. Consequently, these effects must be taken into consideration in the design of optimum separation conditions. While these interactions appear to be complicated they can be used to advantage because the direction and magnitude of EOF can be altered by a change in the nature of electrolyte anion and solvent without the need for the addition of any other compounds. In addition, EOF values were stable over 10 h; normally in the range of ±1–2%.

3.2. Separation of alkali and alkaline earth metal ions

Methanol was chosen initially because of its high dielectric constant, low viscosity and good solvation ability for cations. Acetic acid was chosen as the electrolyte because its cathodic EOF permitted faster separation; EOF in HCl and $HClO_4$ was anodic
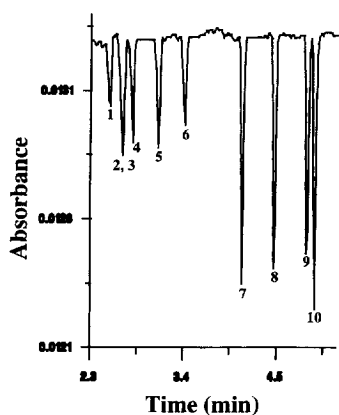
Fig. 4. Separation of alkali and alkaline earth metals and ammonium ion. Experimental conditions: electrolyte, 0.02 mol/l imidazole and 0.03 mol/l acetic acid in methanol; 50 cm capillary (75 μm I.D.) with injection-to-detection length of 43 cm; indirect detection at 214 nm; separation voltage, 20 kV; sample concentration 2×10^{-4} mol/l in water; peak identification, (1) Cs^+, (2) NH_4^+, (3) Rb^+, (4) K^+, (5) Na^+, (6) Li^+, (7) Ba^{2+}, (8) Sr^{2+}, (9) Mg^{2+}, (10) Ca^{2+}.

(counter-flow) and separation currents in both HCl and $HClO_4$ electrolytes were much higher (15–20 times). Imidazole was chosen as the indirect UV absorbance reagent because its mobility is close to
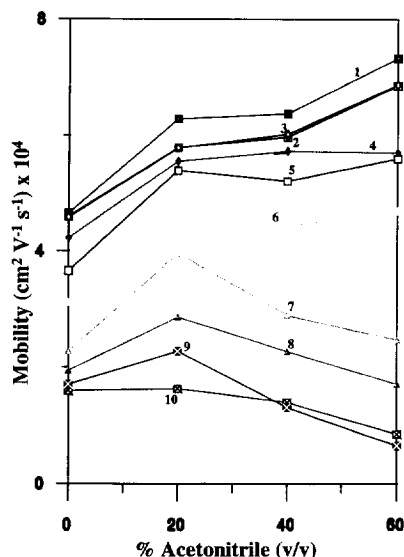

Fig. 5. Effect of the addition of acetonitrile to methanol on separation of alkali and alkaline earth cations; other conditions as for Fig. 4.

alkali and alkaline earth cations, and since it had also been used in the separation of these cations in aqueous media, literature results were available for comparison [11,14]. Tributylbenzylammonium chloride (TBBAC) was also used as an indirect UV reagent but no changes in selectivity relative to imidazole were seen, and because TBBAC moves slower than these metal ions, the peak shapes were poor. The results in Fig. 4 show the separation of nine alkali and alkaline earth cations and ammonium (dissolved in water) in an imidazole/acetic acid electrolyte in methanol. All alkali cations are well separated from alkaline earth cations, and also ammonium and potassium are well separated without the use of any chemical and complexing agents. The complete separation of alkali cations from alkaline earth cations has not been previously reported, and this nonaqueous separation is a unique separation compared to aqueous systems [6–14]. In addition, Li^+, which comes last in aqueous separation of alkali and alkaline metal ions, appears before the alkaline earth cations. Studies on the effect of the concentration of acetic acid on separation selectivity in the range of 0.01 mol/l to 1 mol/l acetic acid showed that migration times increased, but no reversals in separation order were obtained. The maximum change in separation resolution of alkali and alkaline earth cations appeared over 0.01–0.03 mol/l acetic acid. Over this range the mobilities of the alkali cations decreased 1–3% whereas for alkaline earth cations decreases of 10–16% were observed. The larger decrease in mobilities for alkaline earth metals may be attributed to the stronger ion-interaction (ion-pairing and/or complexation) with acetate ions. For the analytes tested, only ammonium and rubidium have almost the same mobility; the choice of other electrolyte systems to produce different amounts of ion-interaction might improve this separation, but this was not examined in these studies.

The effect of the addition of acetonitrile to methanol on the separation selectivity of metal ions was also studied for the imidazole/acetic acid electrolyte. Since alkaline earth cations were not soluble at higher concentration of acetonitrile, the addition of more than 60% v/v acetonitrile was not studied. The results in Fig. 5 show that different trends were observed for alkali and alkaline earth cations. The

decrease in mobilities for alkaline earth cations is likely related to greater ion-interaction for alkaline earth cations upon the addition of acetonitrile. The change in selectivity of Mg^{2+} and Ca^{2+} at ~40% v/v acetonitrile (Fig. 5) could be a result of either stronger ion-interaction (ion-pairing and/or complexation) of Mg^{2+} with acetate ions and/or changes in the relative solvation of these metal ions in the electrolyte. However, there is not enough information in the literature to permit differentiation between these mechanisms. While the changes in selectivity with acetonitrile concentration are not dramatic, the improved separation of alkaline earth ions and the different trends for alkali and alkaline earth metal ions could be used for adjustment of resolution for specific analytical problems.

The reproducibility of migration times were good (%R.S.D.=1 for over 10 h runs) and detection limits were in the range of $7 \times 10^{-6} - 2 \times 10^{-5}$ mol/l for 15 s hydrodynamic injection at 10 cm elevation. Calibration curves gave response factor changes of $\pm 2.5\%$ for Sr^{2+} and $\pm 17\%$ for K^+ over the range of $5 \times 10^{-4} - 5 \times 10^{-5}$ mol/l (correlation coefficients of 0.9997 to 0.994). Separation efficiencies (theoretical plates) were in the range of 155 000–245 000 for alkaline earth cations and 50 000–105 000 for alkali cations (sample concentration 2×10^{-4} mol/l and 5 s hydrodynamic injection at 10 cm elevation). The lower separation efficiencies in the case of alkali cations could be due to the fact that the mobility of imidazole is closer to the mobilities of alkaline earth cations than for alkali cations. To evaluate this system for real samples, it was applied to the separation of metal ions in an aqueous soil extract sample and in a brine solution containing sodium, potassium, calcium and magnesium. Fig. 6 shows the electropherograms for the brine and soil sample solutions. As can be seen, all four metal ions contained in these samples are well resolved and the higher concentration of sodium and potassium (~100 times) did not interfere in the separation.

In conclusion, the above results show that nonaqueous media offer a unique separation selectivity for separation of alkali and alkaline earth and ammonium ions. These ions are sufficiently resolved from each other that the presence of higher concentrations of one or two ions in a mixture should not cause serious overlap with other peaks.
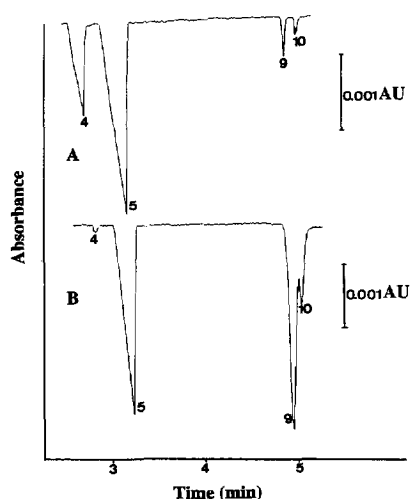

Fig. 6. Separation of alkali and alkaline earth metal ions in (A) a brine solution (280 mg/l NaCl and 130 mg/l KCl in water) and (B) an aqueous soil extract sample; other conditions as for Fig. 4.

Acknowledgments

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