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Journal of Chromatography A, 1068 (2005) 169–174

JOURNAL OF CHROMATOGRAPHY A

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Separation of transition metals in nonaqueous media with capillary electrophoresis

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Abstract

The separation of transition metal Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Fe^{3+} in methanol was investigated by using different types of organic acids as complexing agents. In pure methanol, the weaker and simpler acetic, propionic, butyric and valeric acids could enhance metal ions selectivity by increasing acid concentration and metal ions could be separated with high efficiency. However, hydroxycarboxylic acids obviously made separation efficiency worse. The effect of mixed organic acids, mixture solvent (methanol–acetonitrile, methanol–water) on metal ions separation was discussed further. The advantages of using nonaqueous solvent over aqueous for metal ions separation were shown finally.

Keywords: Nonaqueous capillary electrophoresis; Transition metals; Organic acids

1. Introduction

Capillary electrophoresis (CE) has been developing very rapidly since the 1990s. The number of papers dealing with analysis of metal ions has increased quickly. The traditional approach to the separation of metal ions, ion chromatography (IC), is partially being replaced by CE due to its speed, resolving power, minimal sample and reagent requirements and adaptability to a variety of applications using different separation conditions. The greater simplicity in operation of CE is another advantage. For example, IC requires post-column chelating reagent mixing system for transition metal ions [1], however, the simultaneous separation of routine transition metals, even lanthanide metals with simple indirect detection can be easily achieved with CE [2–9]. The separation process is easily carried out through on-capillary complexation by using weak complexing agents of organic acids.

However, unlike in aqueous, the effect of organic acids in pure organic solvent should be different since the ionization constants of organic acids change in nonaqueous media. Besides that, electrophoretic mobilities of metal ions are also affected due to the interaction between metal ions with polar solvent molecule through ion–dipole bonds. The existence of solvation shell, which is formed around the center ions alters actual size and effective charge of ions, therefore, changes their mobilities. In principle, the solvent solvates all kinds of ions, some to a greater extent than others, depending on the specific properties of the central ion regarding a certain solvent.

Methanol, a protic solvent, is often used in electrolyte to improve the separation selectivity. The favorite amount added is between 5% and 30%, and higher percentage of methanol can cause electrical breakdown [10,11]. However, pure methanol not only changes the acid dissociation constant by many orders of magnitude compared with that in water but also offers potential for adjustment of relative migration rates via change in solvation-ion interaction. So far, only a few articles report the separation of metal ions in pure methanol solvent with acetic acid as complexing agent [2,12,13]. In this paper, nine different types of organic acids (chain acids, hydroxycarboxylic acids and benzoic acid) are investigated for the separation of transition metal Fe^{3+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+}. The influence of mixture solvent (methanol–acetonitrile, methanol–water) on metal ions migration behavior is discussed. The advantages of using non-

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doi:10.1016/j.chroma.2004.10.055

aqueous solvent over aqueous for metal ions separation are shown.

2. Experimental

2.1. Instrumentation

Experiments were performed with a Beckman P/ACE MDQ system (USA), which comprises a CE unit with diode array detector and workstation. Separations were carried out on fused-silica capillaries of 57 cm (50 cm effective length) × 100 μm i.d. (Yongnian Optical Fiber Factory, Heibei, China).

2.2. Chemicals

All reagents were of analytical grade. Metal ion standard stock solutions were prepared by dissolving metal salts $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $ZnCl_2$, $CdCl_2 \cdot H_2O$, $FeCl_3 \cdot 6H_2O$ in methanol of a concentration of 500 μg/ml. Nine organic acids: formic, acetic, propionic, butyric, valeric acid, glycolic, lactic, 2-hydroxyisobutyric acid (HIBA), benzoic acid, and imidazole were from various vendors: Beijing Chemical Company (Beijing, China), Acros Organics and Kanto Chemicals (Tokyo, Japan). Methanol and acetonitrile were of chromatographic grade, purchased from Siyou Biology Medical Co. (Tianjin, China).

2.3. Electrophoretic procedures

The new capillary was rinsed with methanol, water, 1 M HCl and water for 5 min, and then activated with 1 M NaOH and water for 30 min, respectively. Between injections the capillary was rinsed with carrier electrolyte for 3 min. The separation was run at a constant temperature of 25 °C and the voltage applied was 20 kV. The detection wavelength utilized was 191–250 nm. Pressure injection was performed using 0.5 psi for 5 s (1 psi = 6894.76 Pa).

3. Results and discussion

3.1. Influence of organic acids type

Monoprotic organic acids (HA), chain carboxylic acids (formic, acetic, propionic, butyric and valeric acid), hydroxycarboxylic acids (glycolic, lactic, HIBA) and aromatic acid (benzoic acid) were selected as complexing agents. At same acids concentration, ligand A^- concentration was determined by acids dissociation constants pK_a which related to the type of acids (see Table 1). With acids concentration increase, metal ions apparent mobilities changed due to the combined influence of electroosmotic flow (EOF) and complexation. So, the electrophoretic mobilities of metal ions exhibited the complexation degree between metal ions and ligand A^- after eliminating the variant of solution EOF due to acids concentration increase.

Table 1
Organic acid dissociation constants in water

Acid	pK_a
Formic acid	3.751
Acetic acid	4.756
Propionic acid	4.874
Butyric acid	4.871
Valeric acid	4.842
Glycolic acid	3.831
Lactic acid	3.858
HIBA	3.991
Benzoic acid	4.170

3.1.1. Chain carboxylic acid and benzoic acid

In order to testify the effect of carbon chain length on complexation between acids and metal ions, acetic, propionic, butyric and valeric acid were used as complexing agents. According to their pK_a values in water, it could be estimated that their dissociation constants in methanol are very close, so the dissociation situations of their carboxyl which determined the complexing reaction were similar. Our experiments demonstrated that the complexation had no relations to the carbon chain length, the mobilities of metal ions were well in agreement at same acid concentration with above four acids as complexing agents. Fig. 1 shows the influence of propionic acid on mobilities. Mobilities of divalent ions Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} followed the order $Ni^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+}$. With acids concentration increase, their mobilities decreased obviously. The steepness of the decline depended on the magnitude of the formation constants [11]. The reciprocal of their mobilities against the concentration showed straight lines, whose slopes were related to complexing formation constants. From the slopes value, it could be concluded that their formation constants were in the reverse order.

Unlike divalent ions, the mobility of Fe^{3+} exhibited no apparent decrease when acid concentration was increased, which means that nearly no complexation occurred between Fe^{3+} and acids. Considering the charge/size ratio, Fe^{3+} should migrate faster than divalent ions. However, Fe^{3+} had the mobility smaller than Ni^{2+} and Cu^{2+} at low acid concentration (0.05 M). This phenomena demonstrated that the solvation effect changed its charge/size ratio significantly, mobility of Fe^{3+} was dramatically controlled by the solvation of methanol. With propionic acid concentration increasing

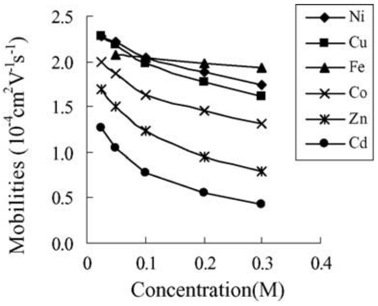

Fig. 1. Dependence of mobilities on propionic acid concentration.