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1,3-Dialkylimidazolium-based room-temperature ionic liquids as background electrolyte and coating material in aqueous capillary electrophoresis

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Abstract

The 1-ethyl-3-methylimidazolium (EMIM) cation was found to have constant mobility of 4.5×10^{-4} cm^2 V^{-1} s^{-1} over the pH range of 3 to 11. The electroosmotic flow of bare silica capillary was reversed by the covalently bonded room-temperature ionic liquid (RTIL) coating. With run buffer of 5 m*M* EMIM (pH 8.5), NH_4^+ in human urine was separated from the K^+ matrix and was detected to be 0.37±0.012%. K^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}, and Ba^{2+} were baseline separated in RTIL-coated capillary with run buffer of 10 m*M* EMIMOH–acetic acid at pH 5, and the concentration of the above ions in a red wine were detected to be 907, 27.9, 0, 71.0, 83.4 and 31.1 μg/ml, respectively. The RTIL-coated capillary showed stable electroosmotic flow for at least 80 h in the run buffer.
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1. Introduction

Room-temperature ionic liquids (RTILs) are those compounds composed of organic cations and inorganic or organic anions which are liquids at room temperature or whose melting points are slightly higher than ambient temperature. In recent decades, their physical–chemical properties were studied in order to develop their applications in low cost electrolytes in rechargeable batteries, photoelectrochemical cells and electroplating, etc. [1,3–8]. Generally, the ionic liquids have the following properties: (1) high ionic conductivity; (2) low vapor pressure; (3) non-flammability; (4) wide electrochemical window and, (5) high thermal stability. The properties of the cation play an important role in determining the melting point of the ionic liquid. 1,3-Dialkylimidazolium and 1-alkylpyridium are common cations composing ionic liquids, while 1,3-dialkylimidazolium-based salts were reported to be the most stable and conductive [2]. The anion can be a halide, $AlCl_4^-$, $CF_3SO_2^-$, BF_4^- or PF_6^-, etc., however, the perfluorinated series anions are usually chosen to lower the viscosity of the salt since the strong delocalization of the negative charge weakens the hydrogen bonding between the cation and anion [2]. Anions also have remarkable influence on the properties of ionic liquids: $EMIMAlCl_4$ is moisture sensitive while $EMIMBF_4$ is water and air stable (EMIM, 1-ethyl-3-methylimidazolium); also for the

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EMIM-based RTILs, the salt composed of BF_4^- is soluble in water but $EMIMPF_6$ is water immiscible. The ionic liquids can be designed with different cations or anions, and more attractively, the R groups of cations can be changed and thus the properties of the compound can be finely tuned for specific purposes [9,13].

Since the late 1990s, EMIM-based ionic liquids have been generating enormous interest in separation science [9–11]. Because they have low volatility, are water and air stable, can be easily and economically prepared, and also because there has been increasing concern about volatile organic compounds (VOCs) in the routine extraction procedures [9,12,13,18], the RTILs are becoming attractive alternatives to organic solvents in liquid–liquid extraction. They have been employed as solvents for catalysts in chemical synthesis because they can provide a highly polar but noncoordinating environment for chemical reactions [9,14–17]. In the work of Armstrong et al., they were employed as stationary phase in gas chromatography (GC) because they can dissolve a number of complex organic molecules [18]. Recently, they were employed as background-electrolyte in non-aqueous capillary electrophoresis (CE) [32]. Their interactions with polyphenols and the capillary wall as well were investigated by Stalcup et al. [33].

CE is an effective way for separating metal ions. Because most of the metal ions are not or weakly UV active, cationic chromophores are usually added into the running buffer for their detection. Most of the currently used cationic chromophores are compounds with atom(s) that can be protonated. Their application as background electrolyte (BGE) is limited to low pH buffer because they will gradually lose the coordinated proton with the increase of pH. The pH of the buffer is one of the most important factors affecting the performance of CE separation; it influences effective mobilities of weak basic or acidic analytes, solubility of some metallic ions as well as electroosmotic flow (EOF). There will be more options to optimize the separating conditions if the BGE can work over a wide pH range.

Another factor concerned with CE is resolution; metal ions are usually separated under capillary zone electrophoresis (CZE) mode and they migrate in the same direction as EOF in the bare silica capillary. By combining the theories of Giddings [22] and Jorgenson [37], the resolution of two zones in CZE, with detecting window in between the ends of the capillary, can be expressed as:

$$\begin{aligned} R &= \frac{\sqrt{N}}{4}\frac{\Delta\mu}{(\overline{\mu}+\mu_{\mathrm{eof}})} \\ &= \frac{\Delta\mu}{4(\overline{\mu}+\mu_{\mathrm{eof}})}\sqrt{\frac{l^2}{2Dt}} \\ &= \frac{\Delta\mu}{4(\overline{\mu}+\mu_{\mathrm{eof}})}\sqrt{\frac{l^2V(\overline{\mu}+\mu_{\mathrm{eof}})}{2DLl}} \\ &= \frac{1}{4\sqrt{2}}\Delta\mu\sqrt{\frac{lV}{DL(\overline{\mu}+\mu_{\mathrm{eof}})}} \end{aligned} \tag{1}$$

where R is the resolution of the neighboring peaks; N is the theoretical plate number; t is the migration time; $\Delta\mu$ is the difference between electrophoretic mobilities of the analytes; V is the separating voltage; D is the diffusion coefficient of the analytes in the buffer; $\overline{\mu}$ is the average electrophoretic mobility of the analytes; μ_{eof} is the EOF, l and L are the effective and total lengths, respectively.

Eq. (1) suggests that EOF affects the separation of analytes: when EOF migrates in the same direction with targets, the resolution will decrease. When they migrate at opposite directions, there is a chance that the resolution between analytes can be improved. The enhancement of the resolution depends upon the difference between EOF and the electrophoretic mobility of the analyte; the highest resolution could be reached when $\mu_{\mathrm{eof}} = -\overline{\mu}$, however the analysis time will be infinite. The EOF of the silica capillary can be reversed by dynamic or static coatings [34–36], in which cationic ions adsorb or covalently bond to the internal capillary surface.

We report in this study the characters of EMIM-based RTILs as background electrolytes and the properties of the RTIL-coated capillary. Our experiments demonstrated that the working pH range of running buffer could be enlarged with good performance using the RTIL as running buffer; the separation of metal ions in the CZE mode improved with an RTIL-coated capillary and a mixture of six metal ions were baseline separated without addition of modifiers usually used in the literature [19,31].

2. Experimental

2.1. Chemicals

Imidazole, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$), 1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIMPF_6$), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIMTFO) and 3-chloropropyltrichlorosilane (CPTCS) were purchased from Fluka (Buchs, Switzerland). 1,2-Dimethylimidazole, 1-ethyl-3-methylimidazolium chloride (EMIMCl) and 1-bromobutane were products of Aldrich (Milwaukee, WI, USA). Dimethyl sulfoxide (DMSO) was obtained from Merck (Darmstadt, Germany). The deionized water in the experiments was prepared by a Milli-Q system (Millipore, Bedford, MA, USA). Purolite A510 (Bala Cynwyd, PA, USA) anion ion-exchange resin was used for preparing EMIM hydroxide (EMIMOH) from EMIMCl. All chemicals were used as obtained unless otherwise stated.

2.2. Apparatus

A laboratory-built system equipped with a Prince CE System (Lauerlabs, Emmen, The Netherlands) and a Linear Instrument (Reno, NV, USA) UVIS 200 detector was employed to perform CE. Electropherograms were recorded with a HP 3394A integrator (Hewlett-Packard, Avondale, PA, USA) or with software (DataApex, Prague, Czech Republic). Electrophoresis was conducted in polyimide-coated fused-silica capillaries of 50 μm I.D. and 360 μm O.D. (Polymicro Technologies, Phoenix, AZ, USA). A Shimadzu (Kyoto, Japan) UV 240 spectrophotometer was used to scan and measure the absorbance of imidazole and EMIM-based ionic liquids. All solutions were filtered with 0.22 μm Millipore filters. Samples were hydrodynamically introduced to the capillary from its anodic side.

2.3. Capillary coating

Imidazolium-based ionic liquid was covalently coated onto the inner surface of fused-silica capillary by the following procedures (see Fig. 1): the fresh capillary was flushed with 1 *M* sodium hydroxide for 2 h followed by deionized water and 1 h of 1 *M* hydrochloric acid. The capillary was then rinsed again with deionized water and methanol for 10 min, respectively. It was flushed with nitrogen gas and heated to 120 °C overnight. In a nitrogen-filled glove box, CTPCS was filtered and introduced into the capillary by positive pressure. The capillary was sealed on both ends and kept at 90 °C for 15 h. After that it was flushed with nitrogen to drive out the unreacted CTPCS, then with toluene. At room temperature, excess imidazole was dissolved in toluene; the upper solution was filtered and introduced into the capillary. The capillary was sealed and kept at 90 °C for desired durations (1, 2, 4, 6, 8, 10 h), then it was rinsed with toluene and dichloromethane progressively and consequently dried with nitrogen at 70 °C for 1 h. It was rinsed with 1-bromobutane for 10 min then sealed and heated at 80 °C for 10 h. The pretreated capillary was rinsed successively with 10 min of toluene, 10 min of

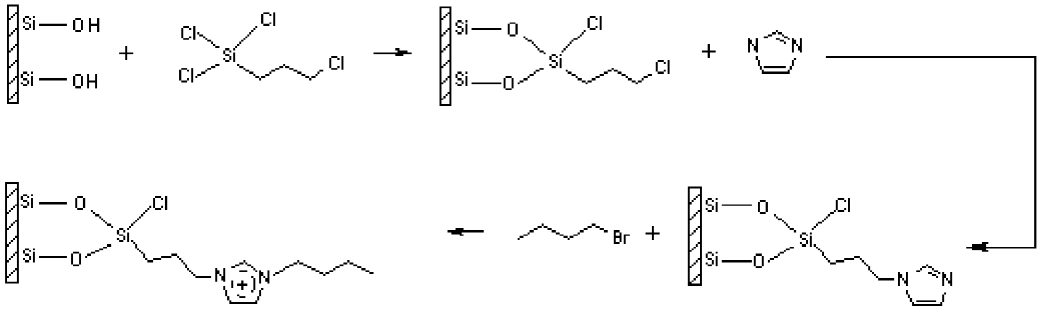


Fig. 1. Scheme representing the IL coating procedure.

methanol and 30 min of deionized water at room temperature before use.

2.4. Preparation of EMIMOH

A column filled with Purolite A510 ion-exchange resin was used during the preparation. The resin was activated by 4 *M* sodium hydroxide solution and rinsed with deionized water till the pH of the eluent was around 7. The EMIMCl solution was loaded and passed through the column at a flow-rate of ca. 1 ml/min. The eluent was collected at pH>13. The concentration of EMIM in the eluent was determined by CE with external standard method.

2.5. Adjustment of pH and calculation of ionic strength

NaH_2PO_4 solutions of known concentrations adjusted to different pH values by 6 *M* NaOH or by 6 *M* H_3PO_4 were employed as buffer electrolytes. Because of the high concentration of NaOH and H_3PO_4, the volume change caused by the pH adjustment was very small and thus could be neglected. The ions in the buffer are $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H^+, OH^- and Na^+. At any given pH and temperature, the fractions of $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and OH^- can be calculated from the fraction equations of phosphoric acid and ionization product of water (the pK_{a1}, pK_{a2} and pK_{a3} of the phosphoric acid used in the calculation were 2.16, 7.2, 12.35, respectively). The concentration of sodium is governed by:

$$[Na^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [OH^-] - [H^+] \quad (2)$$

The formula in square brackets represents the equilibrium concentration of that species in the buffer. The ionic strength can be calculated by $I = 0.5\ \Sigma Z_i^2 C_i$, where, I, Z_i and C_i are ionic strength, charge and concentration of the ion concerned, respectively.

2.6. Preparation of samples and stock solutions

A 100-ml urine specimen was collected from a healthy person. The specimen was diluted with deionized water to 1:5 (v/v) and filtered with a Millipore filter then stored at 5 °C.

The red wines were bought from the local supermarket, and stored at 5 °C. It was diluted with deionized water to 1:15 (v/v), and subsequently sonicated and filtered before experiments.

Standard solutions of K^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}, Ba^{2+} and NH_4^+ of ca. 100 ppm were prepared precisely with deionized water and filtered and then stored at 5 °C. Before analysis, the analytes were further diluted to desired ratios.

3. Results and discussion

3.1. EMIM as background electrolyte

3.1.1. UV absorbance of EMIM in water

At 25 °C, aqueous EMIMCl and imidazole solutions ranging from 1×10^{-5} mol/l to 3×10^{-5} mol/l were prepared and scanned with a spectrometer. EMIM and imidazole show similar absorbance character with absorptivities of 5870 ± 62 $dm^3\ mol^{-1}\ cm^{-1}$ ($n=4$) at 209 nm and 5071 ± 41 $dm^3\ mol^{-1}\ cm^{-1}$ ($n=4$) at 207 nm, respectively.

3.1.2. Mobility

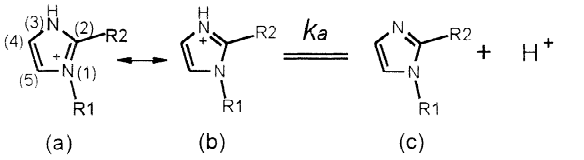
The mobility of species is affected by buffer concentration (ionic strength) and buffer viscosity. In order to eliminate these influences, phosphate buffers of different pH were prepared at equal ionic strength according to the method stated above. The viscosity of the buffers of different pH were measured and all the mobilities were adjusted against viscosity to pH 3 buffer by $\mu_i = \mu_3\eta_i/\eta_3$, where μ_i, μ_3, η_i and η_3 are mobility of the metal ion, mobility of this ion in pH 3 buffer, viscosity of the test buffer and viscosity of the pH 3 buffer, respectively. Mobilities of EMIM-based RTILs composed of different anions, namely, BF_4^-, Cl^-, PF_6^- and TFO, were measured to evaluate the influence of the binding anions.

Table 1 shows that the effective mobilities of imidazole and 1,2-dimethylimidazole decrease remarkably with the increasing pH and drop to zero at pH 9 and pH 10, respectively, while the mobility of EMIM remain relatively stable over the pH range studied. Imidazole and 1,2-dimethylimidazole are weak bases that can be protonated in acidic or

Table 1
Adjusted mobility of EMIM in buffer of different pH

pH	Adjusted mobility (10^{-4} cm^2 V^{-1} s^{-1})					
	Imidazole	1,2-Dimethylimidazole	Anion binding to EMIM			
			Cl^-	BF_4^-	PF_6^-	TFO^-
3	4.76	4.50	4.56	4.67	4.5	4.62
4	4.77	4.50	4.49	4.56	4.61	4.53
5	4.60	4.46	4.52	4.42	4.51	4.43
6	3.95	4.39	4.58	4.42	4.56	4.41
7	2.24	3.78	4.4	4.7	4.39	4.41
8	0.74	2.65	4.72	4.72	4.6	4.69
9	0.08	0.95	4.66	4.65	4.43	4.57
10	0.00	0.22	4.5	4.53	4.5	4.23
11	0.00	0.00	4.34	4.33	4.48	4.77
Average±SD			4.53±0.12	4.56±0.14	4.51±0.07	4.52±0.17

weakly basic solutions. Their dissociation in water can be expressed by [21]:



R1=R2=H: imidazole; R1=R2=CH_3: 1,2-dimethylimidazole

(3)

(a) and (b) in Eq. (3) are two of the resonance forms of imidazole and 1,2-dimethylimidazole, and k_a is the equilibrium constant. The effective mobilities of imidazole and 1,2-dimethylimidazole can be calculated by:

$$\mu_{ef} = \mu_0[H^+]/([H^+] + k_a) \quad (4)$$

Eq. (4) suggests that change of pH will significantly affect the effective mobility of the above weak acids and the compound with larger k_a will suffer more diminution at higher pH.

Both of the imidazole and 1,2-dimethylimidazole rings contain two nitrogen atoms having a lone electron pair. One nitrogen atom contributes its electron pair to the aromatic π system. Another one has its electron pair in an orbital directed away from the ring [21]. This nitrogen atom can be protonated and thus the imidazoles can act as bases. Moreover, in 1,2-dimethylimidazole, the super conjugation effect of the methyl on C(2) makes both of the protonated forms stable. In its resonance form (a), the induction effect of the methyl on N(1) tends to reduce the positive charge, which also contributes to the stability of its protonated form. So 1,2-dimethylimidazole is more basic than imidazole and thus has lower k_a and higher protonation ratio accounting for its higher mobility in basic buffer in spite of its lower charge-to-size ratio. Two factors may account for the stable mobility of EMIM. Firstly, there is no lone electron pair in any carbon or nitrogen atoms in the EMIM cation to be shared by a proton thus it cannot be protonated. Secondly, all hydrogen atoms combine with carbon atoms via covalent bonds; the dissociation constant of the most active hydrogen atoms, those combined to the sp^2 hybridized carbon atoms on the ring, is so small that change of pH cannot produce neutral 1,3-dialkylimidazole of detectable level to affect the mobility.

For EMIM with different anions, the chi square (χ^2) distribution of the four sets of data is $\chi^2 = 0.535$, which suggests no difference among the mobilities according to the χ^2 distribution table [20]. It may imply that these EMIM-based RTILs, although with different anions, are dissociated completely in water.

3.1.3. Influence of buffer concentration

We investigated the interactions between metal ions and RTIL by measuring their effective mobilities. Fig. 2 shows that electrophoretic mobilities of the alkali metal ions are relatively stable with the

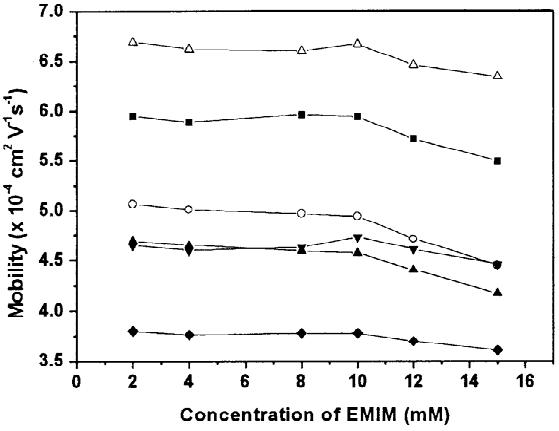


Fig. 2. Influence of EMIM concentration on the electrophoretic mobilities of the metal ions. Buffer, desired concentration of EMIMOH adjusted to pH 4.5 by 2 *M* acetic acid. Fused-silica capillary, 48.0 cm (39.5 cm effective length)×50 μm I.D.×360 μm O.D. Voltage, 10 kV. △, K^+; ▼, Na^+; ♦, Li^+; ○, Ca^{2+}; ▲, Mg^{2+}; ■, Ba^{2+}.

increasing concentration of the EMIM, while the alkaline earth metal ions show more decrease in mobilities from EMIM concentration of 10 m*M* onward. The migration sequence of Na^+ and Mg^{2+} reversed from 8 m*M* EMIM. Also, the effective mobility difference of Ca^{2+} and Mg^{2+} decreases with EMIM concentration. The larger decreases in mobilities suffered by the divalent alkali earth ions than those of the monovalent alkali ions with increasing EMIM concentration may be caused by the ion-pairing effect with acetate whose concentration also increased with that of EMIM. The anodic EOF rate showed slight increase with concentration of EMIM despite the increasing buffer ionic strength and viscosity. We think this might be mainly caused by further adsorption of the imidazolium cation onto the silica wall with more EMIM present in the buffer.

3.2. RTIL-coated capillary

3.2.1. EOF

The EOF of RTIL-coated capillary was reversed because of the cationic surface-bonded imidazolium, while its magnitude decreased with increasing pH value due to further deprotonation of the unshielded surface silanols. The coating procedure parameters also affect EOF; our experiments on reaction time of imidazole with the coated CPTCS indicated that the reversed EOF enlarged with reaction time and reached a maximum with the 8-h reaction, which suggests the maximal coverage of the cation on the capillary surface.

3.2.2. Electrophoresis of metal ions

Both the resolutions of the metal ions and the analysis time are expected to increase in the RTIL-coated capillary because the EOF is reversed. We found that when electrophoresed in the RTIL-coated capillary with a 2-h imidazole–CPTCS reaction and in buffer of 10 m*M* EMIMOH adjusted to pH 5 by acetic acid, the metal ions could be baseline separated within 13 min. The repeatability of retention time (t_m), peak area (A_p) and limit of detection (LOD) are listed in Table 2. The reproducibility of the retention times and peak areas were also evaluated in a 3-day assay. Each day the analyses of fivefold LOD were run in the freshly prepared buffer, the highest relative standard deviation (RSD) of retention time and peak area were 1.3% and 5.3%, respectively. The stability of the RTIL coating was assessed in a 10-day assay (8 h per day) by measuring EOF in the run buffer; the RSD of the EOF was 1.94% ($n=10$).

3.3. Demonstration

3.3.1. Detection of ammonium in human urine

The stable mobility of EMIM may render it some special applications in CE, one of which is indirect UV detection of metal ions in high pH buffer since its mobility is stable in a wide pH range, and is

Table 2
LODs of the analytes and reproducibility of their migration times and peak areas

Metal ion	t_m±SD (min, $n=5$)	RSD% of A_p ($n=5$)[a]	LOD (μg/ml)
K^+	4.75±0.04	2.3	1.2
Na^+	8.19±0.05	4.6	0.4
Li^+	12.54±0.07	3.6	0.08
Ca^{2+}	7.52±0.02	2.3	0.9
Mg^{2+}	8.67±0.07	4.1	0.5
Ba^{2+}	5.60±0.05	2.5	1.9

[a] Concentrations at fivefold LODs each.

closer to those of metal ions compared to the cationic chromophores reported [24,27]. As we know, well-matched mobilities between chromophore and analytes favor high transfer ratios and consequently high sensitivities [25,26].

Ammonium in urine comes chiefly from the decomposition of urea; monitoring ammonium helps to understand the role of the kidney in metabolism and hence is helpful in diagnosing some diseases [28,29]. NH_4^+ is a weak acid ($pK_a = 9.24$). At low pH, it will comigrate with K^+ since they have almost the same mobility [23]. Methods determining NH_4^+ in water include the laborious Kjeldahl titration method, an electrochemical method in which K^+ is still an interfering ion to the electrode [30], a spectrophotometric method which requires expensive instruments and CE with modifiers (such as 18-crown-6) which also have influences on the sensitivity of the analytes. The buffer of this experiment only consists of EMIMOH and phosphoric acid thus the conditions are easy to control. Additionally, fairly high sensitivity can also be expected because no modifier is added. The separation conditions were optimized before analyzing the real sample. The buffer was composed of 5 m*M* EMIMOH adjusted to pH 8.8 by phosphoric acid; the applied voltage was set to 10 kV. The detecting wavelength was 207 nm. Under the above conditions, NH_4^+ is baseline resolved from K^+ and consequently the concentration of K^+ can also be quantitatively determined (Fig. 3). The detection limit (LOD) for NH_4^+ is 2 μg/ml ($S/N = 3$), the linear range is 5–500 μg/ml. Based

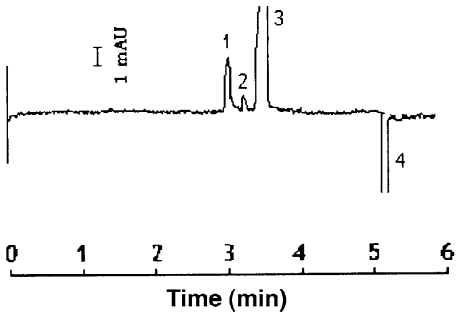


Fig. 3. Determination of NH_4^+ in human urine. Buffer conditions are described in text. The stock solution of urine was further diluted with running buffer until the concentration of urine was 1% (v/v). Peaks: 1, K^+; 2, NH_4^+; 3, Na^+ and Ca^{2+}; 4, EOF. Other conditions as in Fig. 2.

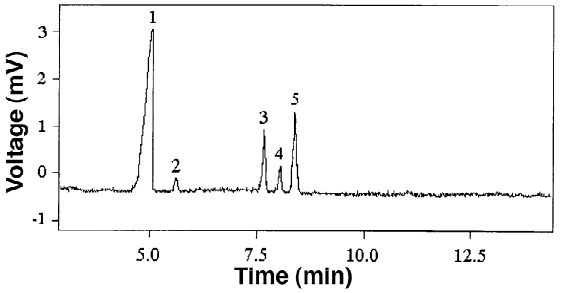


Fig. 4. Electropherogram of red wine samples in RTIL-coated capillary. Buffer, 10 m*M* EMIMOH–acetic acid at pH 5. Capillary: 50 cm (40 cm effective length)×50 μm I.D. Applied voltage, 15 kV. Peaks: 1, K^+; 2, Ba^{2+}; 3, Ca^{2+}; 4, Na^+; 5, Mg^{2+}.

on the external standard method, the concentration of NH_4^+ in urine was determined to be 0.37±0.012% ($n = 5$) from its peak area. It was detected to be 0.34±0.014% ($n = 5$) by Kjeldahl titration for comparison.

3.3.2. Separation and detection of metal ions in red wine

Metal ions can be a fingerprint of wine because they are stable, and they link to factors such as soil, climate, culture and wine-making procedure [31]. The metal ions in a red wine sample were baseline separated (Fig. 4) and their concentrations and the standard deviation (both in μg/ml), calculated from three consecutive runs by peak area with external standard method, were detected as: K^+, 907±11.3; Na^+, 27.9±0.7; Ca^{2+}, 71.0±1.1; Mg^{2+}, 83.4±2.0 and Ba^{2+}, 31.1±1.6.

EMIM-based RTILs with different anions dissociated completely in water. The mobility of EMIM is independent of buffer pH, and hence EMIM can be used as background chromophore in alkaline buffer with good performance. The resolution of metal ions electrophoresed in EMIM-containing buffer in the RTIL-coated capillary are enhanced due to the reversed EOF.

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