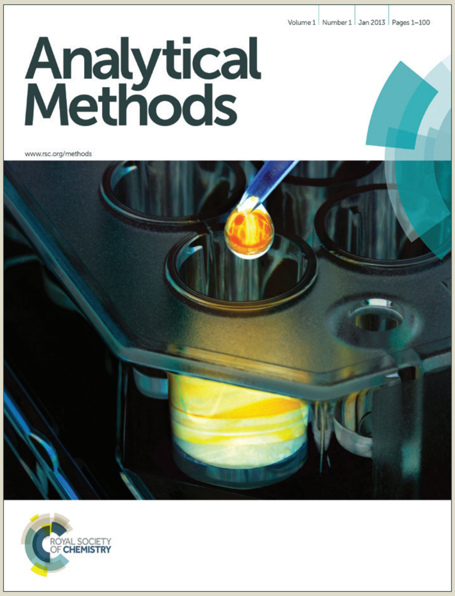
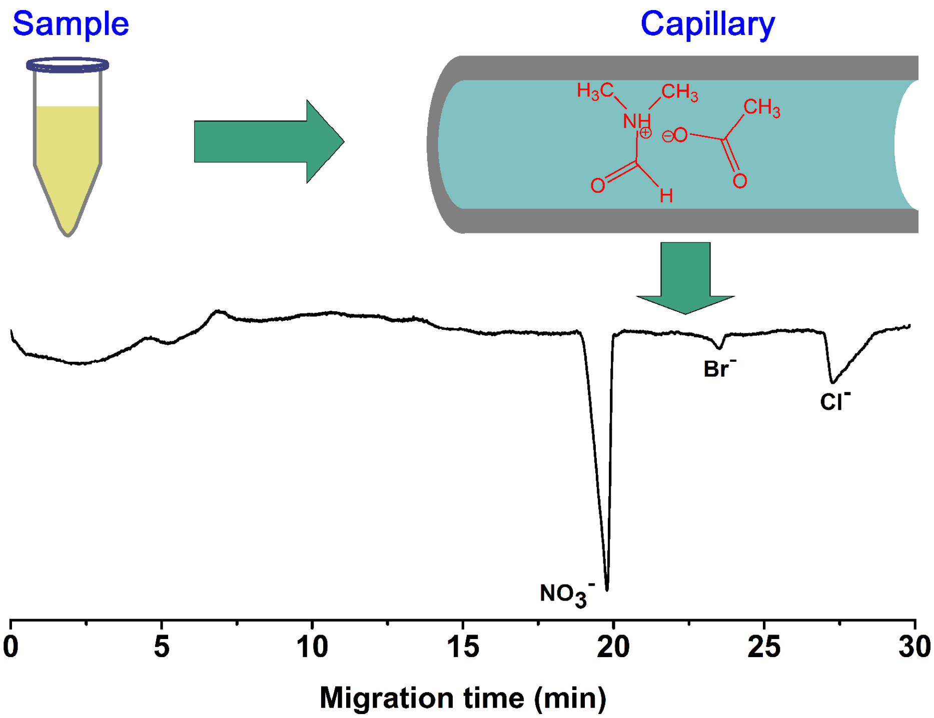
Analytical Methods

Accepted Manuscript



Anions were separated by capillary electrophoresis using a dimethylformamide-acetic acid medium as background electrolyte



Capillary electrophoretic separation of anions in dimethylformamide–acetic acid medium

Zhiren Tian, Weidong Qin *

College of Chemistry, Beijing Normal University, No. 19, Xinjiekou Wai Street, Beijing, 100875, P. R. China

Correspondence:

Dr. Weidong Qin

E-mail: qinwd@bnu.edu.cn

Tel: + 86-10-58802531

Fax: + 86-10-58802075

Key Words: Anions; Nonaqueous capillary electrophoresis; Capacitively coupled contactless conductivity detection; N,N-dimethylformamide

Abstract

A low viscosity, low conductivity medium derived from N,N-dimethylformamide and acetic acid was synthesized and studied for the feasibility as background electrolyte for capillary electrophoresis–capacitively coupled contactless conductivity detection of anions. The background electrolyte could separate anions prepared in solvents of different dielectric constants, polarities, and viscosities, i.e., methanol, acetonitrile, sulfolane and water, with detection limits of 0.83 – 3.83 × 10^{-6} mol/L for BF_4^-, ClO_4^-, PF_6^-, I^-, NO_3^-, Br^- and Cl^-. Finally, the method was applied to determining inorganic anions in tap water and honeys as well as identifying alkyl sulfate surfactants in a shampoo sample.

1. Introduction

Capillary electrophoresis (CE) is a powerful separation tool that offers the advantages of high efficiency and low sample consumption.[1] However, CE separation of small inorganic anions is not a straightforward task because in conventional aqueous buffer, anions migrate from cathode to anode, while the electroosmotic flow (EOF) moves in the reverse direction at a comparable velocity. As a result, the analysis time is long and, even worse, sometimes the high-mobility anions cannot be detected. A number of strategies have been employed to address this problem, such as covalently modifying the capillary surface,[2, 3] dynamically coating capillary with surfactants,[4] or adopting nonaqueous separation media.[5]

Nonaqueous capillary electrophoresis (NACE) is a promising approach because, compared with the aqueous buffer, the organics employed in NACE can provide wider ranges of dielectric constant, polarity, viscosity, and acid/base chemistry.[6] These properties are key buffer parameters affecting separation and should be finely tuned for good CE performances.[7, 8]

Room-temperature ionic liquids (ILs) are salts whose melting points are around the ambient temperature. According to the structures of the cations, they are normally categorized into imidazolium-, pyridinium-, ammonium-, phosphonium- and N,N-dimethylformamide-based ILs.[9, 10] The dialkylimidazolium-based ILs have been widely used in analytical chemistry. Examples include solvents for extraction,[11, 12] stationary phases in high-performance liquid chromatography[13, 14] and gas chromatography,[15] coating materials or buffer additives in aqueous CE,[16-18] and background electrolytes (BGEs) in NACE.[19] However, when serving as BGEs, this kind of ILs have to be dissolved in solvents at millimolar level because they have high conductivities and high viscosities, ordinarily in a range between 35–682 cP.[20] The DMF-based ILs[10] are attractive because they can be prepared by simply mixing DMF and protic acids, and because the raw materials at high purity for the DMF-based ILs are commercially available at reasonable prices. More importantly, some DMF-based ILs have very low viscosity. For instance, the viscosity of $DMFH^+–Ac^-$ was ca. 2 cP as observed by our experiment, much lower than the conventional imidazolium ILs. In addition, we found that $DMFH^+–Ac^-$ possessed low conductivity compared with its analogues in the report.[10] These properties render the material potential separation medium in CE analysis.

We herein investigate, to the best of our knowledge the first time, the feasibility of a DMF-HAc medium, $DMFH^+–Ac^-$, as background electrolyte for separation and detection of anions, viz., $BF_4^–$, $ClO_4^–$, $PF_6^–$, $I^–$, $NO_3^–$, $Br^–$, $Cl^–$ and some alkyl sulfates ($C_{12}H_{25}SO_4^-$ and $C_{16}H_{33}SO_4^-$), by CE–capacitively coupled contactless conductivity detection (C^4D). Among the analytes, $I^–$, $NO_3^–$, $Br^–$ and $Cl^–$ are common ions at considerable contents in seawater, ground water and, in some areas, drinking water. Alkyl sulfates ($C_nH_{2n+1}SO_4^-$) are widely used in synthetic detergents.

Hexafluorophosphates are often used as antimicrobial compounds, and tetrafluoroborates are important chemicals in plating industry. Perchlorates are strong oxidants at high temperature; besides being used for military purpose as key ingredients in dynamite, they are widely used in production of fireworks. These ions can enter ground water via domestic and/or industrial sewage. Consequently, analytical methods have to be developed not only to monitor quality of the products but to evaluate their influence on the environment. CE has also been applied to this field; nonetheless, indirect photometric detection was usually employed because most of these ions lack chromophores. Conductivity detection (CD) is a universal detection approach, sensitivity of which is dependent on mobilities of the species monitored and the background co-ion. C^4D, a CD approach, is a competitive alternative to the conventional on-column optical detection methods because it does not rely on particular chromophores or fluorophores, neither does it have the disadvantage of short path length encountered by the optical detection techniques. In this report, factors influencing the separation performance were studied, and the applicability of the method was demonstrated by determining inorganic anions in tap water and honeys and identifying organic anions in a shampoo sample.

2. Experimental

2.1 Reagents

DMF, acetic acid (HAc), sodium fluoroborate, sodium chloride, sodium nitrate and ammonium hexafluorophosphate were purchased from Sinopharm Chemicals (Beijing, China). Sodium bromide and potassium iodide were products of Bodi Chemicals (Tianjin, China). Sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) and sodium hexadecyl sulfate ($C_{16}H_{33}SO_4Na$) were from Sigma (St. Louis, MO, USA). All the other chemicals were of the highest quality available.

2.2 Synthesis of DMF-HAc medium

The DMF-HAc medium was synthesized by slightly modification of a previous report.[10] Briefly, the reaction was carried out under vigorous stirring in a round-bottom flask chilled by ice-water bath. A volume of 20.0 mL DMF was added to the flask and was neutralized by slow, dropwise addition of equimolar glacial acetic acid (14.80 mL). The product was dried by rotary evaporation at 70 °C under reduced pressure to remove water and the minor reactant residues, leaving behind the desired product.

2.3 Conductometric titration

In a titration cell thermostated at 25 °C, 25 mL glacial acetic acid was magnetically stirred, to which aliquots of DMF was added stepwise with a pipette. After each addition, conductance of the solution was recorded with a DDS–11A conductometer (Hongyi Instrument, Shanghai, China). The corrected conductance of each addition was obtained by multiplying the reading with a factor f, $f = (V+V_0)/V_0$, where V_0 is the starting volume of the solution (glacial acetic acid) and V the accumulated volume of the titrant.

2.4 Fourier transform infrared (FTIR) experiments

Infrared spectra of the DMF-HAc medium and the fresh DMF-HAc mixture were recorded with a resolution of 4 cm^{-1} on a Nicolet 380 FTIR spectrometer (Thermo Electron Corporation, Waltham, MA, USA) at room temperature. A 2 cm × 1.5 cm poly(methyl methacrylate) plate was used for sample loading. Background subtraction was performed in order for the acceptable accuracy and reproducibility. A total of 100 interferograms were accumulated over the spectral range of 4000 – 500 cm^{-1} to ensure good signal-to-noise ratio.

2.5 Sample solutions

Acacia honey (Classic Brew, Shanghai, China), date honey (Bao Chun Tang, Chongqing, China), vitex honey (Chang He, Yunnan, China) and shampoo (Rejoice, Guangzhou, Guangdong, China) were bought from a local supermarket. Individual solutions of each honey sample were prepared by dissolving precisely weighed 4 g honey in 10 mL deionized water (Millipore, Bedford, MA, USA). The shampoo sample was diluted 100-fold with deionized water. Tap water taken from the laboratory was used without dilution. Before injection, all sample solutions were filtered through 0.22 µm filters (Jiuding High Tech., Beijing, China).

Recoveries (R%) of analytes from the sample solutions were estimated according to

$$R\% = \frac{S_2 - S_1}{S_0} \times 100 \tag{1}$$

where S_1 and S_2 are the peak areas of an anion in unspiked and spiked sample solutions, respectively, and S_0 the peak area of this anion prepared in deionized water at the spiking concentration.

2.6 Capillary electrophoresis

Experiments were performed on a CE system consisting of a high-voltage power supply (Sanchuan High Tech., Tianjin, China) and an in-house made C^{4}D detector. The detector was described previously.[21] Briefly, two 5 mm × 0.5 mm i.d. stainless steel needles were employed, one acting as actuator electrode and another as pick-up electrode. The electrodes were separated by a copper foil and were shielded by a grounded copper housing. During measurement, an oscillation voltage was applied on the actuator electrode by a function generator (YSD996A, Peiming, Jiangsu, China). The signal reflecting the conductivity of the gap between the electrodes was collected by a data acquisition unit (CT22, Qianpu, Jiangsu, China) and subsequently processed with HW2000 chromatography station (Qianpu). A 60 cm (50 cm in effective length) 75 µm i.d. bare fused-silica capillary (Ruifeng Photoconduction Fiber, Hebei, China) was employed for separation. The new capillary was conditioned for 1 hour with 0.5 M NaOH (prepared in methanol/water, 50:50, v/v), 20 min with methanol, and was finally purged for 30 min with pure nitrogen. Every day before experiments, the capillary was flushed for 10 min with BGE. Typically, injections were performed hydrodynamically by lifting the injection end to a height of 20 cm for 30 s. The injection plug length was estimated using a free software distributed by Beckman Coulter (Fullerton, CA, USA). Separations were carried out under negative voltages. The viscosity of the DMF-HAc medium was measured by the method proposed by Francois et al.[22]

3. Results and discussion

3.1 Characterization of the DMF-HAc medium

The viscosity of the DMF-HAc medium was measured to be 2 cP, significantly lower than the reported values of 35–682 cP for the widely used dialkylimidazolium-based ILs.[22]

3.1.1 Conductometric titration

Fig. 1 depicts that the conductivity of the mixture increased with addition of DMF to HAc until $n_{\mathrm{DMF}} / n_{\mathrm{HAc}} \approx 0.5$, after which the conductivity reduced. Liquid acetic acid existed predominantly as cyclic dimmers ($(\mathrm{HAc})_2$);[23] addition of DMF facilitated the dissociation of the dimmer ($(\mathrm{HAc})_2 \rightarrow \mathrm{H}^+ + \mathrm{HAc}_2^-$) by forming the protonated DMF (DMFH^+) and, consequently, increased the conductivity of the mixture. DMF and Bronsted acid formed 1:1 salt[10] (in this paper, denoted as DMFH^+–Ac^-), but, as revealed by the low conductivity (7.15 $\mu\mathrm{S}\cdot\mathrm{cm}^{-1}$ versus 280–2810 $\mu\mathrm{S}\cdot\mathrm{cm}^{-1}$ for the analogues in the report[10]), the dissociation constant of the complex was very low. This may be the consequence of cohesive intra-complex electrostatic forces which led to ion pairing/association, and of van der Waals interactions as well.[10]

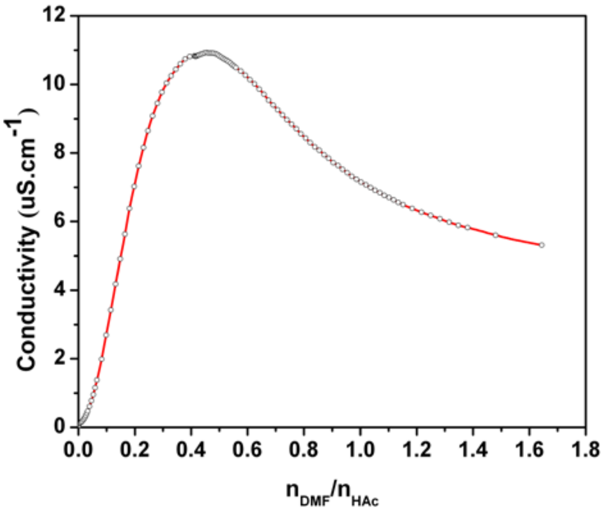


Fig. 1 Conductivity variation of DMF-HAc binary mixture as a function of molar ratio

3.1.2 IR spectra

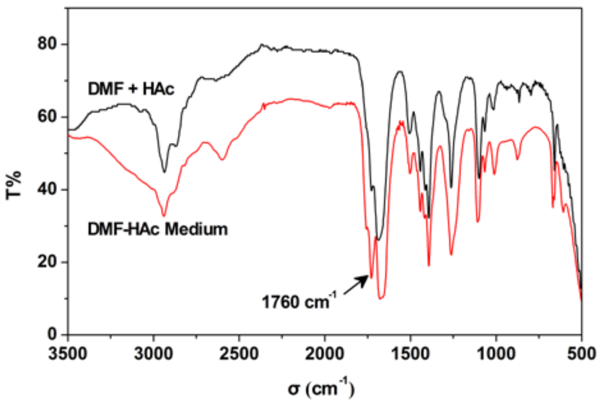


Fig. 2 FTIR spectra of fresh DMF/HAc and DMF-HAc complex

The fresh DMF/HAc mixture was tested within 5 min after mixing

The FTIR spectrum of DMF-HAc medium (Fig. 2) shows a new band at 1760 cm^{-1}, which, according to the existing report,[10] was assigned to C=N stretch of the cation

(DMFH$^+$). Our results are coincident with the previous report that DMFH$^+$ could exist in both keto and enol forms[24] (the two structures were illustrated in Scheme S1 of the Supporting Information).

The experiments suggest that the product contained the DMFH$^+$–Ac$^-$ complex and its dissociation components, DMFH$^+$ and Ac$^-$, concentrations of which were low but played important roles in CE performances as will be demonstrated in the ensuing experiments. Although such acetic acid-based acid-base complexes at low ionicity can be sometimes called "ionic liquids" [25, 26], we think it is safe to term the product used in this work "DMF-HAc medium" since the dissociation degree of the complex was very low.

3.2 CE performances of the DMF-HAc media at different initial DMF/HAc ratios

DMF, HAc and the DMF-HAc media prepared from DMF-HAc mixtures at different molar ratios were investigated as BGEs for CE separation of inorganic anions, i.e., BF_4^-, ClO_4^-, PF_6^-, I^-, NO_3^-, Br^- and Cl^-. Under the separation voltage, the currents across the capillary were so low that the reading fluctuated between 0–1 μA (this phenomenon was observed throughout the experiments in this report). No peaks could be observed with DMF or HAc (traces A and B of Fig. 3). Regarding the DMF-HAc media, the migration times of the anions reduced with decreasing DMF/HAc molar ratio due to the improved "acidity" of the mixture and, therefore, more DMFH$^+$ adsorbed to the silica surface, leading to enhanced anodic EOF. The best separation was achieved at the DMF/HAc ratio of 1:1, at which the DMFH$^+$–Ac$^-$ complex was stoichiometrically formed (here, we term it the stoichiometrically complexed DMF-HAc BGE, s-BGE). At lower DMF/HAc ratios (traces F and G), higher content DMFH$^+$ existed in the separation medium and/or on the capillary surface, and migration of bromide and chloride might be impeded by their electrostatic interaction with DMFH$^+$.

The s-BGE showed distinct characters from the conventional aqueous BGEs. The electroosmotic flow of the capillary filled with s-BGE was reversed owing to the wall-adsorption of DMFH$^+$, being -3.2×10^{-5} cm^2·V^{-1}·s^{-1}. The mobilities of the anions were in the range of -8.1×10^{-5}– -1.42×10^{-4} cm^2·V^{-1}·s^{-1}, far less than those in water solution. The halides, Cl$^-$, Br$^-$ and I$^-$, which had close mobilities in aqueous buffer and were often overlapped in conventional CE without additives,[27] were well separated in s-BGE.

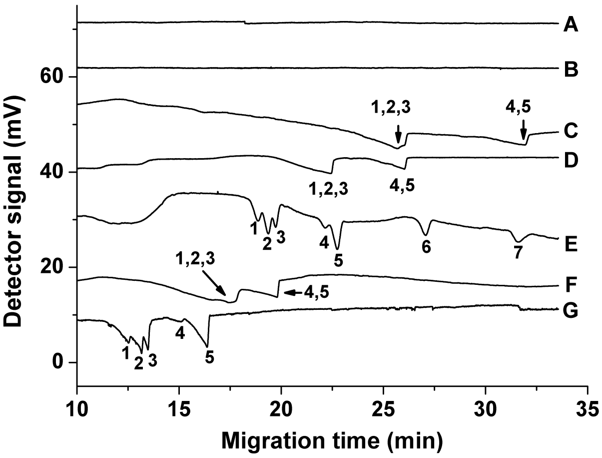


Fig. 3 Influence of DMF/HAc molar ratio

The BGEs: A, DMF; B, HAc; C, 4:1; D, 2:1; E, 1:1; F, 1:2; G, 1:4. Peak identities: 1, BF_4^-; 2, ClO_4^-; 3, PF_6^-; 4, I^-; 5, NO_3^-; 6, Br^-; 7, Cl^-. Separation voltage: -14 kV. The C^4D excitation conditions: 100 kHz × 20 $V_{p\text{-}p}$. Traces were offset for clarity.

3.3 Influence of sample solvents

Four solvents, methanol, acetonitrile, sulfolane and deionized water, were used to prepare the standards. To obtain clear electropherograms, six ions, i.e., BF_4^-, PF_6^-, I^-, NO_3^-, Br^- and Cl^-, were selected this time. Our preliminary experiments found that the baseline noise was high with sulfolane as sample solvent. Therefore, the injection time was increased to 40 s for recognizable peaks, and this time was applied to all standards for comparison. The electropherograms were similar with all the solvents (Fig. 4A). However, the detection sensitivity was the highest for the anions prepared in acetonitrile, and was the lowest in water. Moreover, the solvents notably affected migration of the anions, especially for the low-mobility species (Fig. 4B). For example, unlike the fronting peaks for other ions, the peak shape of chloride prepared in water was a tailing triangle due to the low mobility. Further, comparison of Fig. 3 and Fig. 4A reveals that with longer injection time the migration window, the migration time difference between the first and the last peaks, narrowed for aqueous standards.

The total migration time of an ion was the sum of the migration time in the injection zone, which was surrounded by the sample solvent, and the migration time in the s-BGE until it reached the detector. The migration velocity of the ion in the injection zone was dictated by the sample solvent properties, such as permittivity and viscosity (Table S1). High viscosity of the injection zone hindered the migration and therefore resulted in long analysis time. High sample solvent permittivity resulted in high conductivity of the plug and, as a consequence, low local electric field and slow migration velocity. Another factor should be concerned regarding the migration in the injection zone is the change in local conductivity and viscosity upon DMF-HAc complex entering the zone, by either electrophoretic migration or diffusion. Dissociation of the DMF-HAc complex in sample solvent led to improvement in local conductivity because one of the products, acetic acid, would partly deprotonate. Our experiments revealed that the anions migrated at lower mobilities in the injection zone than in the s-BGE (Section 3 of the Supporting Information). When the ion electrokinetically migrated across the interface, from the sample zone to the s-BGE, the desolvation (from the sample solvent) and the solvation (with the s-BGE) of the ion took place simultaneously.[28] The process changed the properties of the ion, imposing effect on the mobility. The long sample plug with low local electric field during separation and the desolvation/salvation process might be responsible for the mobility changes of the ions.

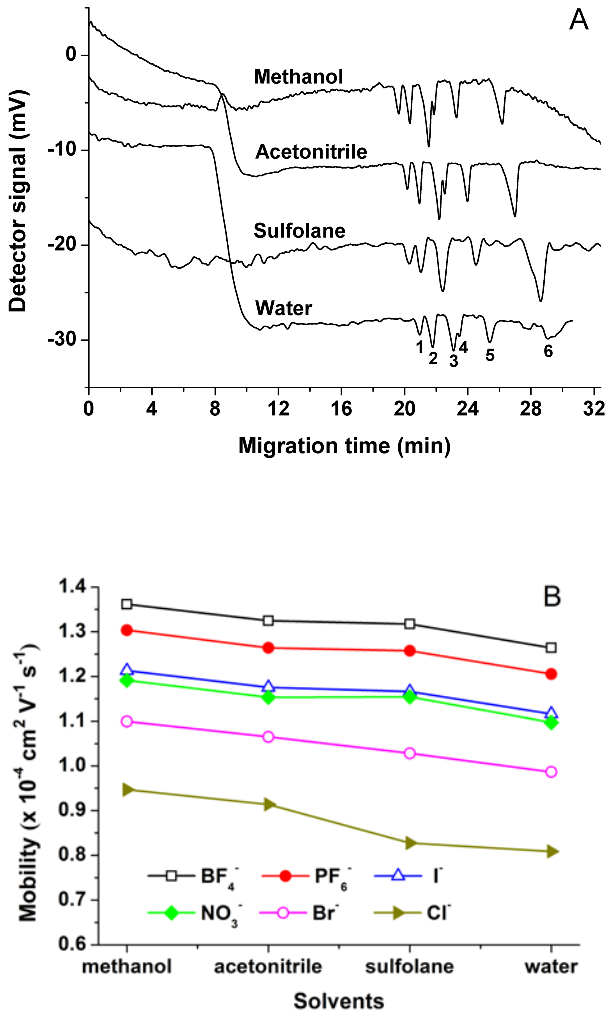


Fig. 4 Influence of sample solvents on the electropherograms (A) and mobility of ions (B). The experiments were carried out in s-BGE. Standard solutions were injected at 20 cm × 40 s; separation voltage was -15 kV. The peaks: 1, BF_4^-; 2, PF_6^-; 3, I^-; 4, NO_3^-; 5, Br^-; 6, Cl^-. Other conditions were the same as Fig. 3.

3.4 Influence of the C^4D parameters

The influence of oscillation frequency on the C^4D detection was investigated in the range of 30–500 kHz. The intensity of anion peaks first increased with the frequency, reaching maximum at 100 kHz, then decreased at higher frequencies (Fig. 5). At low excitation frequency, the capacitive reactance is a pronounced factor impeding sensitive detection;[29] at high frequency, however, the increased stray capacitance between the electrodes reduced the response of C^4D.[30]

The effect of oscillation amplitude of the signal generator was investigated between 8–20 V. Our experiments indicated that peak heights increased proportionally with excitation voltage (Fig. S2). Therefore, the highest output voltage of 20 Vp–p was employed.

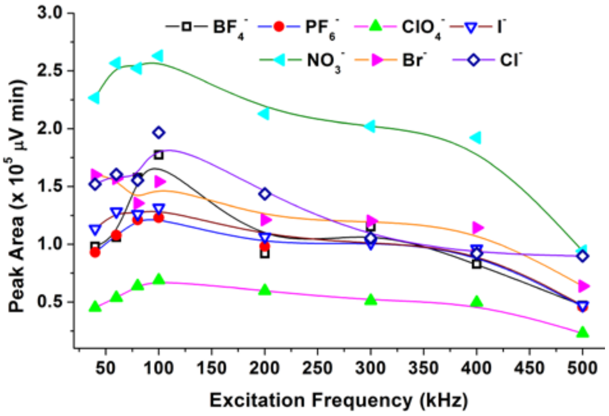


Fig. 5 Influence of oscillation frequency

Data were obtained based on aqueous standards; the excitation frequency varied between 30 and 500 kHz; standard solutions were injected at 20 cm × 40 s. Other conditions were the same as Fig. 4.

3.5 Performance and demonstration

Under the optimized conditions, i.e., anions being separated in s-BGE, detected by

C^4D with excitation frequency at 100 kHz and excitation voltage at 20 V, good linearities were obtained for all anions in the concentration ranges studied, with correlation coefficients (r^2 values) higher than 0.99 (Table 1). The limits of detection (LODs, S/N = 3, in 10^{-6} mol/L) for BF_4^-, ClO_4^-, PF_6^-, I^-, NO_3^-, Br^- and Cl^- prepared in acetonitrile were calculated to be 3.83, 1.80, 0.83, 2.93, 3.68, 2.54 and 2.47, respectively. The sensitivity is higher than those obtained by CE-UV.[31, 32] The precisions of migration times and peak areas were studied in terms of intraday repeatability, which was based on five consecutive injections (n = 5), and in interday reproducibility, which was estimated on three consecutive days (n = 3×5 = 15). The intraday and interday variabilities of the migration time, expressed in relative standard deviations (RSDs), were no more than 3.41% and 3.10%, respectively. The corresponding values for peak areas were no more than 9.60% and 9.96%, respectively. The RSDs were comparable with our previous report using C^4D detection.[21] Note that the experiments were performed on laboratory-made CE system. We think the precisions can be improved by using more sophisticated commercial CE instrument, for example, equipped with autosampler (for peak areas) and able to operate under constant current mode (for migration times).

The typical electropherograms of the honey and tap water samples are presented in Fig. 6A. Table 2 lists the recoveries of the standard addition method and the anion contents in the samples. The high recoveries, 92.4–103.1%, suggest that the method can quantitatively determine anions in these samples. The noticeable variability of anion contents in honeys might be due to the different botanical origins. The concentration of nitrate in the laboratory tap water (98.1 mg/L, equal to 22.1 mg/L in nitrogen) was slightly higher than the critical value of 20 mg/L (nitrogen) set by the National Standards for Drinking Water Quality (GB 5749-2006),[33] because the water was not treated for drinking purpose. Fig. 6B indicates that the surfactants in the shampoo sample could be detected by CE–C^{4}D. We spiked the sample solution with two alkyl sulfate surfactants, $C_{12}H_{25}SO_4$ and $C_{16}H_{33}SO_4$, and two peaks were identified. The small side peaks (8' and 9') suggest that positional isomers may exist.

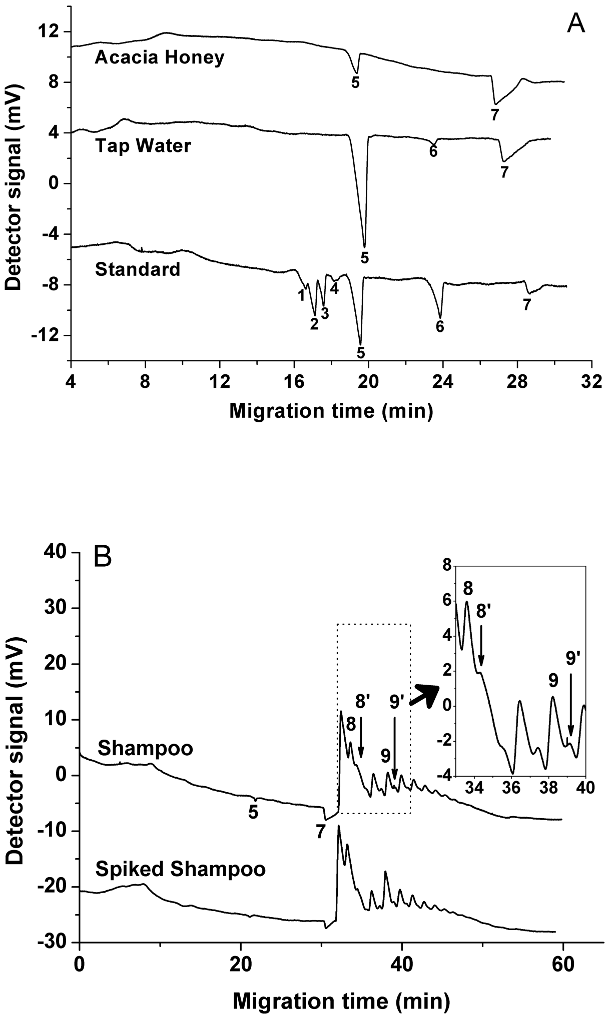


Fig. 6 Representative electropherograms of honey and tap water (A) and shampoo (B).

Samples were analyzed with s-BGE. Separation voltage: A, -14 kV; B, -18 kV. In panel B, $C_{12}H_{25}SO_4Na$ and $C_{16}H_{33}SO_4Na$ were fortified at 0.5 mM each in the spiked shampoo sample. Samples were injected at 20 cm × 30 s. Peak identities: 8, $C_{12}H_{25}SO_4^-$; 9, $C_{16}H_{33}SO_4^-$. Other conditions were as trace E of Fig. 3.

Table 1 Figures of merit of the method [a]

	Anions						
	BF_4^-	ClO_4^-	PF_6^-	I^-	NO_3^-	Br^-	Cl^-
Linear range (10^{-5} mol/L)	1.0–20.0	1.0–20.0	0.5–10.0	0.8–12.0	1.0–15.0	1–25.0	0.8-20.0
Intercept ($\times 10^4$ μV·min)	2.57±1.16	1.08±0.65	4.73±1.13	0.98±0.59	1.88±0.77	2.67±1.15	2.03±0.97
Slope ($\times 10^4$ μV·min /mM)	1.82±0.06	3.75±0.03	4.65±0.08	3.00±0.02	2.78±0.03	1.53±0.05	1.63±0.06
r^2	0.9961	0.9959	0.9902	0.9965	0.9910	0.9941	0.9987
LOD (10^{-6} mol/L)	3.83	1.80	0.83	2.93	3.68	2.54	2.47
LOD[b] (10^{-5} mol/L)	1.15	0.63	0.44	1.23	1.14	1.93	1.90
Intra-day precision (RSD%, n=5) at 3 × 10^{-4} mol/L [b]							
Migration time	2.48	2.54	2.62	2.63	2.43	3.41	2.90
Peak area	7.32	9.60	8.08	8.10	6.76	5.86	6.23
Inter-day precision (RSD%, 3 days, n = 3×5 = 15) at 3 × 10^{-4} mol/L [b]							
Migration time	2.42	1.26	2.40	2.38	2.51	2.99	3.10
Peak area	5.95	6.30	7.48	9.96	5.63	6.58	8.95

[a] unless otherwise stated, all parameters were based on standards prepared in acetonitrile

[b)] standards were prepared in water

Table 2 Recoveries and concentrations of anions in honeys and tap water

Sample	Recovery ±SD (%, n = 3) / Concentration spiked			Concentration determined [a]		
	Cl^-	Br^-	NO_3^-	Cl^-	Br^-	NO_3^-
acacia honey	98.9±0.8/100.0	99.2±0.8/10.0	99.0±0.7/10.0	107.4	N. D.[b]	6.0
date honey	92.4±6.0/40.0	103.1±2.0/10.0	97.5±1.3/10.0	31.1	N. D.	15.3
vitex honey	96.5±1.7/40.0	97.2±0.9/10.0	98.4±0.7/10.0	34.8	N. D.	20.1
tap water	99.2±5.0/40.0	100.1±6.0/10.0	101.4±4.3/100.0	31.4	10.9	98.1

[a] mg/kg for honeys and mg/L for tap water; [b] below LOD

4. Conclusions

It is well known that conventional ionic liquids, when used in CE as BGEs, should be dissolved in solvents at millimolar levels for low Joule heating and ease of operation. Because of its low conductivity and low viscosity, the new complex of $DMFH^+–Ac^-$ can be directly used as BGE, in which anion standards prepared in different solvents could be successfully separated and detected. Moreover, the DMF-HAc medium was applied in determining anions in tap water and honey samples as well as in identifying anionic surfactants in detergent. Our experiments suggest that the DMF-HAc media are potential BGEs for CE analysis.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20975014) and the Fundamental Research Funds for the Central Universities.

Notes and references

1. S. Namur, M. Gonzalez-de la Parra and G. Castaneda-Hernandez, *J. Chromatogr. B*, 2010, **878**, 290-294.

2. J. J. Stine and C. P. Palmer, *J. Sep. Sci.*, 2009, **32**, 446-456.

3. M. Borissova, M. Vaher, M. Koel and M. Kaljurand, *J. Chromatogr. A*, 2007, **1160**, 320-325.

4. S. T. Garcia, M. I. A. Valenzuela and E. P. Gil, *Talanta*, 2008, **75**, 748-752.

5. A. Rousseau, M. Pedrini, P. Chiap, R. Ivanyi, J. Crommen, M. Fillet and A. C. Servais, *Electrophoresis*, 2008, **29**, 3641-3648.

6. A. C. Servais, M. Fillet, P. Chiap, W. Dewe, P. Hubert and J. Crommen, *Electrophoresis*, 2004, **25**, 2701-2710.

7. S. Palonen, S. P. Porras, M. Jussila and M. L. Riekkola, *Electrophoresis*, 2003, **24**, 1565-1576.

8. P. B. Wright, A. S. Lister and J. G. Dorsey, *Anal. Chem.*, 1997, **69**, 3251-3259.

9. P. Sun and D. W. Armstrong, *Anal. Chim. Acta*, 2010, **661**, 1-16.

10. J. F. Huang, G. A. Baker, H. M. Luo, K. L. Hong, Q. F. Li, N. J. Bjerrum and S. Dai, *Green Chem.*, 2006, **8**, 599-602.

11. A. B. Pereiro and A. Rodriguez, *Green Chem.*, 2009, **11**, 346-350.

12. C. H. Zhou, S. S. Tong, Y. X. Chang, Q. Jia and W. H. Zhou, *Electrophoresis*, 2012, **33**, 1331-1338.

13. K. R. Chitta, D. S. Van Meter and A. M. Stalcup, *Anal. Bioanal. Chem.*, 2010, **396**,

775-781.

14. Y. Huang, S. Yao and H. Song, *J. Chromatogr. Sci.*, 2013, **51**, 739-752.

15. J. L. Anderson and D. W. Armstrong, *Anal. Chem.*, 2003, **75**, 4851-4858.

16. W. D. Qin, H. P. Wei and S. F. Y. Li, *J. Chromatogr. A*, 2003, **985**, 447-454.

17. L. J. Yu, W. D. Qin and S. F. Y. Li, *Anal. Chim. Acta*, 2005, **547**, 165-171.

18. L. B. Li, H. W. Du, H. Yu, L. Xu and T. Y. You, *Electrophoresis*, 2013, **34**, 277-283.

19. M. Vaher, M. Koel and M. Kaljurand, *J. Chromatogr. A*, 2002, **979**, 27-32.

20. C. F. Poole and S. K. Poole, *J. Chromatogr. A*, 2010, **1217**, 2268-2286.

21. Z. J. Yang and W. D. Qin, *J. Chromatogr. A*, 2009, **1216**, 5327-5332.

22. Y. Francois, K. Zhang, A. Varenne and P. Gareil, *Anal. Chim. Acta*, 2006, **562**, 164-170.

23. James M. Briggs, Toan B. Nguyen and W. L. Jorgensen, *J. Phys. Chem.*, 1991, **95**, 3315-3322.

24. L. Zhang, H. R. Li, Y. Wang and X. B. Hu, *J. Phys. Chem. B*, 2007, **111**, 11016-11020.

25. K. M. Johansson, E. I. Izgorodina, M. Forsyth, D. R. MacFarlane and K. R. Seddon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2972-2978.

26. J. Stoimenovski, E. I. Izgorodina and D. R. MacFarlane, *Phys. Chem. Chem. Phys.*, 2010, **12**, 10341-10347.

27. D. Kaniansky, V. Zelenska and D. Baluchova, *Electrophoresis*, 1996, **17**, 1890-1897.

28. S. P. Porras, M. L. Riekkola and E. Kenndler, *Electrophoresis*, 2003, **24**, 1485-1498.

29. T. Chvojka, I. Jelinek, F. Opekar and K. Stulik, *Anal. Chim. Acta*, 2001, **433**, 13-21.

30. J. G. A. Brito-Neto, J. A. Fracassi da Silva, L. Blanes and C. Lucio do Lago, *Electroanalysis*, 2005, **17**, 1198-1206.

31. N. Bord, G. Cretier, J. L. Rocca, C. Bailly and J. P. Souchez, *J. Chromatogr. A*, 2005, **1100**, 223-229.

32. W. P. Yang and Z. J. Zhang, *Anal. Lett.*, 2003, **36**, 465-477.

33. Standardization Administration of China, *Standards for Drinking Water Quality (GB5749-2006)*, July 2007.