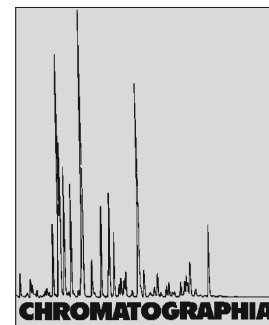


LC Analysis of Hexafluorophosphate on a Monolithic Column: Application to the Analysis of Ionic Liquids



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Abstract

A silica-based monolithic column with tetrabutylammonium hydroxide–phthalic acid–acetonitrile as mobile phase has been used for LC analysis of hexafluorophosphate with direct conductivity detection. The effects of mobile phase composition, column temperature, and flow rate on retention of hexafluorophosphate were investigated and the optimum chromatographic conditions were selected. Common anions and tetrafluoroborate did not interfere with analysis of hexafluorophosphate. The detection limit ($S/N = 3$) for hexafluorophosphate was 6.2 mg L^{-1} . Relative standard deviation ($n = 5$) for peak area was 0.1%. The method was successfully used for analysis of hexafluorophosphate in ionic liquids.

Keywords

Column liquid chromatography
Monolithic column
Conductivity detection
Ionic liquids
Hexafluorophosphate

Introduction

Hexafluorophosphate (PF_6^-) is an important anion in ionic liquids, which are, chemically, salts of, often, a small inorganic anion (bromide, chloride, tetrafluoroborate, or hexafluorophosphate) and a bulky asymmetric organic cation (for example

the dialkylimidazolium, alkylpyridinium, or alkylammonium). Ionic liquids are molten at room or low temperature [1, 2]. Recently, with the emergence and development of green chemistry, applications of ionic liquids in organic synthesis, catalysis, analytical chemistry, etc., has become very extensive [1, 3–5].

In the process of preparation and application of ionic liquids, analysis of cations or anions can be used to determine the kind and the purity of the liquids and the presence of impurity ions. There have been few reports of analysis of the anions in ionic liquids. Villagrán et al. [6] and Hao et al. [7] analyzed halide anions in ionic liquids by ion chromatography (IC) with suppressed conductivity detection. Two methods have been used by Zhou et al. for analysis of BF_4^- in ionic liquids. The first was based on anion-exchange separation by IC with direct conductivity detection [8]. The second used high-performance liquid chromatography (LC) with a monolithic column [9].

Hexafluorophosphate is also widely used as an electrolyte in lithium-ion batteries. Its purity has a substantial effect on the energy, life, and safety of the battery [10]. It is, therefore, very important to develop an effective method for its analysis. Polarography [11], IC, and LC are the main methods for analysis of PF_6^- . Du et al. [12] analyzed PF_6^- in electrolyte solution by IC. Kazakevich et al. [13] studied the adsorption isotherms of hexafluorophosphate on four LC columns.

In recent years, the preparation and application of monolithic columns have

developed rapidly in LC and IC [14, 15]. The main forms of monoliths are organic polymer and silica-based. Two methods are used to separate anions on silica-based monolithic columns. In one method an ion-pair reagent is added to the mobile phase and the ion pairs are then separated by LC [16, 17]. In the other method the monolith is modified with cationic surfactant or latex to create ion-exchange sites with which the analytes can interact, and the ions are then separated by IC [18, 19].

In this work, a silica-based monolithic column was used, for the first time, for analysis of PF_6^- by LC with direct conductivity detection. Factors affecting retention of PF_6^- were investigated and the optimum chromatographic conditions were selected, enabling rapid analysis of PF_6^- in ionic liquids.

Experimental

Reagents

Tetrabutylammonium hydroxide (TBA) as a 25% (w/w) solution in water was obtained from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Hexafluorophosphate, tetrafluoroborate, chloride, bromide, and fluoride, used as their sodium salts to prepare standard solutions, and acetonitrile and phthalic acid were supplied by J&K Chemical (Beijing, China). All reagents were analytical grade or LC grade. Ionic liquids used as the samples were purchased from Shanghai Chengjie Chemical. (Shanghai, China).

Solutions were prepared in $18.2 \text{ M}\Omega \text{ cm}^{-1}$ deionized distilled water from a Millipore (Bedford, MA, USA) Milli-Q water-purification system. Before injection, solutions were filtered through a $0.22\text{-}\mu\text{m}$ membrane filter (Automatic Science, Shanghai, China). Stock standard solutions of concentration $1,000 \text{ mg L}^{-1}$ were prepared monthly. Working standard solutions were prepared daily, as required, from the respective stock solutions.

Milli-Q water was also used to prepare mobile phases. Aqueous TBA solution and acetonitrile were mixed in the appropriate proportions, then phthalic

acid was added to adjust the pH. A model PHSF-3F pH meter (Shanghai Precision and Scientific Instrument, Shanghai, China) was used for pH measurement. Before use, mobile phases were filtered through a $0.22\text{-}\mu\text{m}$ membrane filter, then degassed for 15 min with a model DOA-P504-BN pump (IDEX, CHI, USA).

Chromatography

All experiments were conducted with an LC-20A ion chromatograph (Shimadzu, Kyoto, Japan) comprising an LP-20ADsp liquid-delivery pump, CDD-10Avp conductivity detector, SIL-20A autosample injector, CTO-20AC column oven, and SCL-10Avp system controller. The column and conductivity detection cell were placed inside the CTO-20AC column oven for temperature control. The exact column temperature was controlled to within $0.1 \text{ }^\circ\text{C}$. Chromatograph control, data acquisition, and data analysis were performed by means of an LC solution Ver 1.1 workstation (Shimadzu).

All separations were performed on a $50 \text{ mm} \times 4.6 \text{ mm}$ i.d. Chromolith Speed ROD RP-18e C_{18} -bonded column (Merck, Darmstadt, Germany). The optimized mobile phase used for the separation consisted of 0.5 mmol L^{-1} TBA + 0.48 mmol L^{-1} phthalic acid + 5% acetonitrile (pH 6.0). The flow rate was 6.0 mL min^{-1} . Column temperature was $35 \text{ }^\circ\text{C}$. Injection volume was $20 \text{ }\mu\text{L}$. Direct conductivity detection was used. To eliminate hydrophobic TBA adsorbed by the column, the column should be flushed with at least 30 mL water-acetonitrile 95:5 (v/v) every day, after analysis.

Results and Discussion

Effect of Mobile Phase Acetonitrile Content on the Retention of Hexafluorophosphate

In this part of the investigation, the flow rate was 3.0 mL min^{-1} , the column temperature was $30 \text{ }^\circ\text{C}$, and the mobile phase was 0.5 mmol L^{-1} TBA

containing 1, 3, 5, 7, or 9% acetonitrile adjusted pH 5.5 with phthalic acid. The retention factor of PF_6^- decreased from 49 to 26 when the concentration of acetonitrile was increased from 1 to 9%. There are two mechanisms of separation:

- the ion-pair reagent (TBA) is dynamically adsorbed by the stationary phase, creating ion-exchange sites, and retention takes place by ion-exchange between the anion (PF_6^-) and adsorbed counter cation (TBA);
- TBA associates with the PF_6^- to form a neutral ion pair and retention takes place by hydrophobic interaction between the neutral ion pairs and the stationary phase.

With increasing concentration of acetonitrile the surface tension of the mobile phase reduced, which in turn reduces solvophobic adsorption of the neutral ion pair on the stationary phase, which reduces retention. Simultaneously, acetonitrile also elutes TBA adsorbed on the stationary phase. In both cases, with increasing concentration of acetonitrile, the retention factor of PF_6^- decreases. To reduce consumption of acetonitrile, the appropriate acetonitrile concentration selected was 5%.

Effect of Mobile Phase pH on the Retention of Hexafluorophosphate

The effect of mobile phase pH on the retention factor of PF_6^- was investigated using a column temperature of $30 \text{ }^\circ\text{C}$ and a flow rate of 3.0 mL min^{-1} . Mobile phases of pH 4.5, 5.0, 5.5, 6.0, and 6.5 were prepared by addition of phthalic acid to a solution comprising 0.5 mmol L^{-1} TBA + 5% acetonitrile. When the pH was changed from 4.5 to 6.5, the retention factor of PF_6^- increased from 32 to 38, i.e. the retention factor of PF_6^- varied slightly with changing pH within this range of acidity. As already mentioned, the retention mechanism includes ion exchange. The phthalate ion was used in the mobile

phase, and consumption of phthalic acid decreased with increasing pH, which may result in weakening eluent strength, so the retention factor of PF_6^- increased with the increasing pH. When the pH was 6.0, PF_6^- had a low retention factor and a well-shaped peak was obtained, so pH 6.0 was chosen as suitable.

Effect of TBA Concentration on the Retention of Hexafluorophosphate

In this part of the investigation, flow rate was 5.0 mL min^{-1} and column temperature was $30 \text{ }^\circ\text{C}$. Mobile phases containing 5% acetonitrile and 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, or 2.0 mmol L^{-1} TBA were prepared, and then adjusted to pH 6.0 with phthalic acid (the corresponding concentrations of phthalic acid were 0.16, 0.48, 0.52, 0.60, 0.66, 0.72, 0.79, and 0.91 mmol L^{-1} , respectively). The retention factor of PF_6^- increased from 26 to 64 when the TBA concentration was increased from 0.25 to 2.0 mmol L^{-1} . On the basis of the two mechanisms of retention discussed above, the quantity of TBA adsorbed on the surface of the column increases with increasing TBA concentration, leading to larger ion-exchange capacity. Thus, retention of PF_6^- increases in accordance with the anion-exchange mechanism. Likewise, formation of neutral ion pairs is enhanced with increasing concentration of the ion-pair reagent (TBA), which strengthens the hydrophobic interaction between neutral ion pair and stationary phase. So the retention of strongly retained analytes (PF_6^-) increases, in accordance with the hydrophobic interaction mechanism. The peak shape of PF_6^- deteriorated when the TBA concentration exceeded 1.25 mmol L^{-1} . When the TBA concentration was 0.5 mmol L^{-1} , the retention time of PF_6^- was relatively short and the background conductivity of the mobile phase was low, so a TBA concentration of 0.5 mmol L^{-1} was appropriate for a phthalic acid concentration of 0.48 mmol L^{-1} .

Table 1. Effect of flow rate on retention time and retention factor of hexafluorophosphate, and on column back-pressure, and column efficiency

Parameter	Flow rate (mL min^{-1})					
	1	2	3	4	5	6
Retention time (min)	23.7	12.7	8.0	6.1	4.9	4.2
Retention factor	31.2	31.5	31.7	32.4	33.1	33.2
Column back-pressure (MPa)	3.4	4.9	6.1	7.3	8.3	9.1
Effective plate height (μm)	32.1	33.6	38.4	38.7	40.7	41.9

Effect of Flow Rate on the Retention Time of Hexafluorophosphate, Column Back-Pressure, and Column Efficiency

During investigation of the effect of flow rate, the mobile phase used was 0.5 mmol L^{-1} TBA + 0.48 mmol L^{-1} phthalic acid + 5% acetonitrile (pH 6.0), the column temperature was $30 \text{ }^\circ\text{C}$, and the flow rate was varied from 1.0 to 6.0 mL min^{-1} . Changes of retention time, retention factor, column back-pressure, and column efficiency with changing flow rate are listed in Table 1. The results show that the retention time of hexafluorophosphate obviously decreases with increasing flow rate. At a flow rate of 6.0 mL min^{-1} , separation time is the shortest with a stable baseline. The retention factor of hexafluorophosphate changed little with increasing flow rate. Although column back-pressure increased with increasing flow rate, at a flow rate of 6.0 mL min^{-1} , or even higher, the pressure was still lower than conventional LC operating pressure. Column efficiency changed slightly with increasing flow rate. These results showed that the monolithic columns used for LC analysis of hexafluorophosphate have the advantages of speed and high efficiency.

Effect of Column Temperature on Retention of Hexafluorophosphate

In this part of the research, the mobile phase was 0.5 mmol L^{-1} TBA +

0.48 mmol L^{-1} phthalic acid + 5% acetonitrile (pH 6.0) and the flow rate 6.0 mL min^{-1} . When column temperatures of 25, 30, 35, and $40 \text{ }^\circ\text{C}$ were investigated the retention time of PF_6^- decreased slightly with increasing temperature. The relationship between retention and temperature in chromatography follows the Van't Hoff equation [20–22]:

$$\ln k = -\Delta H/RT + \Delta S/R + \ln \Phi$$

where k is the retention factor, T the temperature (Kelvin), ΔH the enthalpy change, ΔS the entropy change, R the universal gas constant, and Φ the column phase ratio. Regression data were obtained for a plot of $\ln k$ against $1/T$ ($\times 10^3 \text{ K}^{-1}$) for PF_6^- at different temperatures. The slope ($-\Delta H/R$) of the Van't Hoff plot was 0.7537, with a correlation coefficient of 0.9962. This positive slope indicates that retention of PF_6^- is an exothermic process. When the column temperature was $35 \text{ }^\circ\text{C}$ the retention time of PF_6^- was relatively short, and a well-shaped peak was obtained. So a column temperature of $35 \text{ }^\circ\text{C}$ was appropriate.

By combining the results discussed above, the optimum chromatographic conditions chosen for analysis of PF_6^- were 0.5 mmol L^{-1} TBA + 0.48 mmol L^{-1} phthalic acid + 5% acetonitrile (pH 6.0) as mobile phase, flow rate 6.0 mL min^{-1} , and column temperature $35 \text{ }^\circ\text{C}$. A chromatogram obtained from a standard mixture of PF_6^- , BF_4^- , and other common anions (F^- , Cl^- , Br^- , and NO_3^-) under these conditions is shown in Fig. 1. The retention time of hexafluorophosphate was less than 5 min; BF_4^- and the other common anions did not interfere with the analysis.

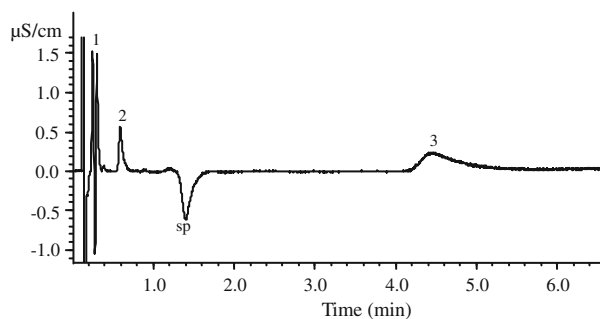


Fig. 1. Chromatogram obtained from hexafluorophosphate, tetrafluoroborate, and some common anions. Chromatographic conditions: Chromolith Speed ROD RP-18e column; mobile phase 0.5 mmol L^{-1} TBA + 0.48 mmol L^{-1} phthalic acid + 5% acetonitrile (pH 6.0); flow rate 6.0 mL min^{-1} ; column temperature $35 \text{ }^\circ\text{C}$; injection volume $20 \text{ }\mu\text{L}$; direct conductivity detection. **1** = F^- , Cl^- , Br^- , and NO_3^- (the concentration of each anion was 10.0 mg L^{-1}), **2** = BF_4^- (20.0 mg L^{-1}), **3** = PF_6^- (80.0 mg L^{-1}), **sp** = system peak

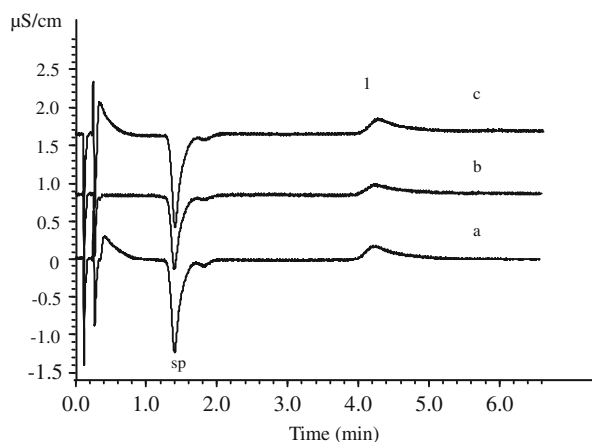


Fig. 2. Chromatograms obtained from ionic liquids. **a** 1-butyl-3-methylimidazolium hexafluorophosphate; **b** 1-octyl-3-methylimidazolium hexafluorophosphate; **c** 1-propyl-2,3-dimethylimidazolium hexafluorophosphate. **1** = PF_6^- , **sp** = system peak. Chromatographic conditions as for Fig. 1

Table 2. Analytical results and recoveries of hexafluorophosphate in ionic liquids

Ionic liquid	Original, ρ_o (mg L^{-1})	Added, ρ_A (mg L^{-1})	Found, ρ_F (mg L^{-1})	Recovery, R (%)	Amount in ionic liquid, w (%)
BMIM PF_6	40.54	30.0	70.87	101.1	32.67
OMIM PF_6	34.78	30.0	64.85	100.2	30.20
PDMIM PF_6	38.10	30.0	67.42	97.7	31.22

BMIM PF_6 1-butyl-3-methylimidazolium hexafluorophosphate, OMIM PF_6 1-octyl-3-methylimidazolium hexafluorophosphate, PDMIM PF_6 1-propyl-2,3-dimethylimidazolium hexafluorophosphate

Quantitative Data

Detection limit, regression data, and precision were obtained by analysis of a series of standard solutions of PF_6^- under the optimized chromatographic conditions. Relative standard deviation

(RSD) of chromatographic peak area obtained by repeated measurement of a standard solution containing 80 mg L^{-1} PF_6^- was 0.1% ($n = 5$). The detection limit for PF_6^- , i.e. the amount for which the signal-to-noise ratio (S/N) was 3, was 6.2 mg L^{-1} . Response (peak area) was a

linear function of PF_6^- concentration in the range 10 to 200.0 mg L^{-1} . The linear regression equation for the calibration plot was:

$$y = 109.2x + 3.7$$

where y is the integrated peak area and x is the concentration of PF_6^- , expressed in mg L^{-1} . The correlation coefficient ($n = 5$) was 0.9999.

Sample Analysis

The method was applied to analysis of PF_6^- in three ionic liquids—1-butyl-3-methylimidazolium hexafluorophosphate, 1-octyl-3-methylimidazolium hexafluorophosphate, and 1-propyl-2,3-dimethylimidazolium hexafluorophosphate. Precisely known amounts of the ionic liquids (0.1–0.2 g) were diluted to 100 mL with water–acetonitrile 95:5 (v/v) as stock solutions and 3 mL of the stock solutions were diluted to 50 mL. The latter solutions were filtered through $0.22\text{-}\mu\text{m}$ membrane filters and used for analysis of PF_6^- under the optimized chromatographic conditions. The chromatograms obtained from the ionic liquids are shown in Fig. 2. Recoveries were tested by use of the standard addition method; the results obtained (average results from five measurements) are listed in Table 2. The RSD of the analytical results were less than 3.0%. Recoveries of PF_6^- after spiking were 97.7–101.1%. These results indicate the method has the advantages of high accuracy and good precision, and it has been successfully used for quantitative analysis of PF_6^- in ionic liquids.

Conclusions

A method has been developed for separation and analysis of PF_6^- by high-performance liquid chromatography on a silica-based monolithic column with direct conductivity detection. The retention time of hexafluorophosphate was less than 5 min. BF_4^- and common anions (F^- , Cl^- , Br^- and NO_3^-) did not interfere with analysis of hexafluorophosphate. The experimental results are

discussed in depth on the basis of two mechanisms of retention—ion exchange and hydrophobic interaction. The concentrations of TBA and acetonitrile in the mobile phase had significant effects on the retention factor of PF_6^- , which decreased with increasing acetonitrile concentration and increased with increasing TBA concentration. Mobile phase pH and column temperature had little effect on the retention factor of PF_6^- . The method was used for analysis of PF_6^- in ionic liquids. The analytical results were accurate and reliable.

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