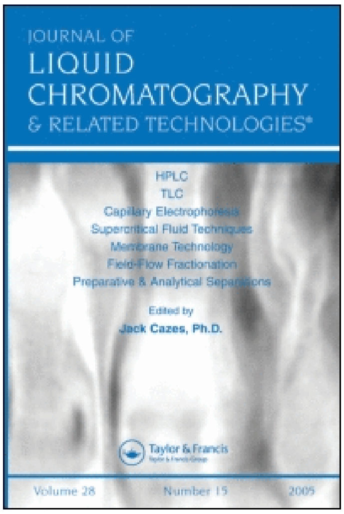

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DETERMINATION OF IMIDAZOLIUM AND PYRIDINIUM IONIC LIQUID CATIONS BY ION CHROMATOGRAPHY

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☐ *We investigated the effect of concentration and pH of methanesulfonic acid, as well as volume percent of acetonitrile, in the mobile phase mixtures on retention of imidazolium and pyridinium cations as test analytes by ion chromatography. Analyses were performed on a cation exchange column employing crown ether and carboxylate and phosphonate cation exchange sites. Isocratic elution mode was applied. The IL cations eluted by 2.5, 5, 7.5, and 9 mM MSA followed the elution order typical for reversed phase HPLC if acetonitrile up to 60% (v/v) was used. Changes of elution order differed if IL cations were eluted by 1 mM MSA. Especially using a higher percentage of acetonitrile, in excess of 65% (v/v), the analytes showed normal phase HPLC retention behavior. With increasing MSA concentration, i.e., decreasing pH, the retention of IL cations decreased. Two concentrations of MSA, 2.5, and 5 mM were chosen to separate IL cations. Unfortunately, cations, such as EEIM, PMIM, and BEIM, MBPy and EBzMIM, HMPy, HMIM were not separated properly. The low percentage of acetonitrile can help to separate EEIM and PMIM, but simultaneously longer analysis times preclude the detection of HMPy, HMIM and OMIM because of peaks bordering.*

Keywords hydrophobic interactions, ion chromatography, ion exchange, ionic liquid cations, retention mechanism, separation

INTRODUCTION

Ionic liquids are known since 1914.[1] They are molten salts with a melting point often below 100°C.[2–4] Ionic liquid structure consists frequently of large and asymmetric, organic cations and anions of lower-molecular mass. Most frequently used cations are: imidazolium, pyridinium,

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ammonium, while anions are tetrafluroborate, hexafluorophosphate, chloride and bromide.[2–4] Ionic liquids were considered as green solvents for the last few years because of their extremely low vapor pressure. They have, however, many other favorable properties, such as: viscosity, high thermal and chemical stability, solubility of starting materials and other solvents, high ionic conductivity, wide temperature range for liquid phase.[4–6] For those reasons ionic liquids have been introduced to different scientific areas, such as organic synthesis and catalysis, electrochemistry, photochemistry, extraction, tissue preservation, solar cells, separation techniques.[7,8]

Wide application of ionic liquids requires development of methods of determination. They should allow ionic liquid purity determination to control the technological process, in which those salts are synthesized or used as solvents.[9] On the other hand, optimized analytical methods may be utilized in the monitoring of the environment, if ionic liquids will enter water or soils.[9]

Several techniques have been used for the separation or qualitative and quantitative determination of ionic liquids. They were analyzed with capillary electrophoresis (CE),[10,11], isotachophoresis,[12] high performance liquid chromatography (HPLC),[13–16] and ion chromatography (IC).[17] Each of those techniques appeared to have its advantages and disadvantages for ionic liquids separation or determination. Cations with identical molecular masses or of low hydrophobicity are not separable in CE; their separation with HPLC is also unsatisfactory, although the quantitative analytical performance of developed methods was excellent. The best selectivity in the separation of polar cations is characteristic for IC.[11,13,17]

In IC, ion exchange resins are used to separate ions based on the charge properties of molecules. Coulombic interactions are the most influential in the retention mechanism of ions.

The first study devoted to the separation of sodium and 1-methyl-3-ethylimidazoilum cations with a cation exchange column by IC was presented by Stuff et al.,[17] whereas anion exchangers were applied in the quantification of halides in imidazolium, pyridinium, and pyrrolidinium ionic liquids, since the content of those anions can significantly affect ionic liquid properties and usefulness.[18,19] It was proven that IC is a reliable technique, which provides a convenient method for the determination of chloride, bromide, or iodine impurities in ionic liquids. The last two studies devoted to the analysis of ionic liquids with the use of IC focus on cation determination.[20,21] Stepnowski et al. studied concerns about the analytical parameters (mobile phase pH, buffer concentration, amount of organic modifier) performance in the analysis of several imidazolium ionic liquids.[20] The key matter in ionic liquids determination is, however, simultaneous analysis of cations and anions. The first study related to this subject was presented last year. A tandem of columns containing cation and anion exchangers followed by conductometric detection was used. It was shown that the developed method is simple and selective.[21]

The main aim of the present research was to investigate ionic liquid cations retention in the IC system with cation exchange packing. Eleven 1,3-dialkyl-, 1-aryl-3-methylimidazolium and pyridinium cations were chosen for this purpose. The influence of acetonitrile in the mobile phase, as well as the concentration of methanesulfonic acid and its pH on the retention factor of studied cations, was investigated. On the basis of obtained data, preliminary conditions for ionic liquid cations separation in isocratic elution were selected.

EXPERIMENTAL

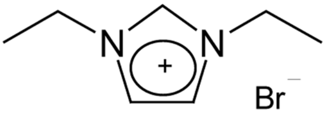
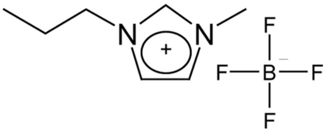
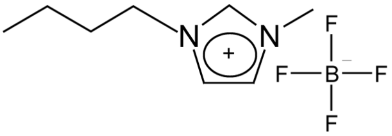
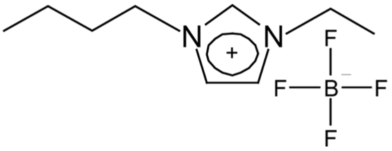
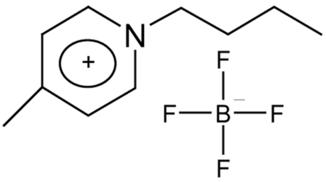
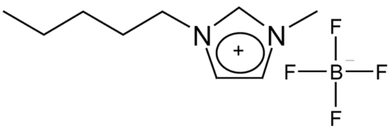
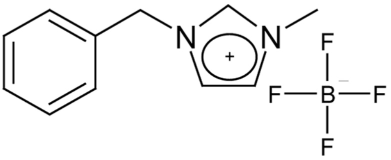
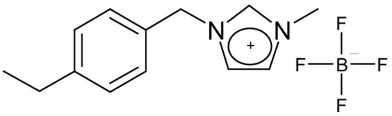
Instrumentation

All the chromatographic analyses were performed with an ion chromatograph Dionex, model ICS-3000 consisting of an autosampler, a degasser, a pump, a thermostat, a conductometric detector, and a personal computer with Chromeleon Chromatography Management software to process data collection and analysis as well as to automate sample injection and eluent generation (Dionex Corporation, Sunnyvale, CA, USA). The Dionex micromembrane suppressor CMMS 300 (4 mm) was installed between the analytical column and conductometric detector. The cations of IL were analyzed on a Dionex IonPac CS15 column (4 × 250 mm, 8.5 μm) consisting of macroporous polymers ethylvinylbenzene crosslinked with 55% divinylbenzene and functionalizing with carboxylate and phosphonate cation exchange sites and crown ether groups. The Dionex guard column IonPac CG15 (4 × 50 mm) was also employed. The pH measurements were done with a pH meter CP-505 (Elmetron, Zabrze, Poland). Water was prepared with a Milli-Q Purification system (Millipore, Bedford, MA, USA) and KOH for suppressor regeneration were filtered using a PTFE Membrane 0.2 μm filter (BGB Analytik AG, Boeckten, Switzerland). The analytical scale RADWAG XA 60/220/X (Radwag, Radom, Poland) was used for KOH solution preparation.

Samples and Chemicals

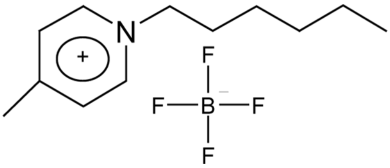
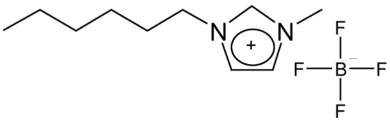
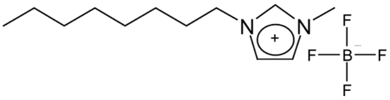
Standards of ionic liquids were obtained from Merck (Merck, Darmstadt, Germany) and from the collection of Prof. B. Jastorff (University of Bremen, Germany), synthesized in the laboratory of

TABLE 1 Structure, Abbreviation, Molecular Mass and Hydrophobicity Parameter of IL Cations used Under the Under Investigation

Systematic Name	Abbreviation	Structure	Molecular Mass	log P
1-ethyl-3-ethylimidazolium bromide	[EEIM] [Br]		205	0.15
1-*n*-propyl-3-methylimidazolium tetrafluoroborate	[PMIM] [BF_4]		212	0.28
1-*n*-butyl-3-methylimidazolium tetrafluoroborate	[BMIM] [BF_4]		226	0.68
1-*n*-butyl-3-ethylimidazolium tetrafluoroborate	[BEIM] [BF_4]		240	1.02
1-butyl-4-methylpyridinium tetrafluoroborate	[MBPy] [BF_4]		237	1.68
1-*n*-amyl-3-methylimidazolium tetrafluoroborate	[AMIM] [BF_4]		240	1.07
1-benzyl-3-methylimidazolium tetrafluoroborate	[BzMIM] [BF_4]		260	0.48
1-(*p*-ethylbenzyl)-3-methyl-imidazolium tetrafluoroborate	[EBzMIM] [BF_4]		288	1.03

(*Continued*)

TABLE 1 Continued

Systematic Name	Abbreviation	Structure	Molecular Mass	log P
1-hexyl-4-methylpyridinium tetrafluoroborate	[HMPy] [BF_4]		265	2.47
1-*n*-hexyl-3-methylimidazolium tetrafluoroborate	[HMIM] [BF_4]		254	1.47
1-*n*-octyl-3-methylimidazolium tetrafluoroborate	[OMIM] [BF_4]		282	2.26

Prof. B. Ondruschka (University of Jena, Germany), and were as follows: 1-ethyl-3-ethylimidazolium bromide (EEIM), 1-n-propyl-3-methylimidazolium tetrafluoroborate (PMIM), 1-n-butyl-3-methylimidazolium tetrafluoroborate (BMIM), 1-n-butyl-3-ethylimidazolium tetrafluoroborate (BEIM), 1-n-butyl-4-methylpyridinium tetrafluoroborate (MBPy), 1-n-hexyl-4-methylpyridinium tetrafluoroborate (HMPy), 1-benzyl-3-methylimidazolium tetrafluoroborate (BzMIM), 1-n-amyl-3-methylimidazolium tetrafluoroborate (AMIM), 1-(p-ethylbenzyl)-3-methylimidazolium tetrafluoroborate (EBzMIM), 1-n-hexyl-3-methylimidazolium tetrafluoroborate (HMIM), 1-n-octyl-3-methylimidazolium tetrafluoroborate (OMIM). Concentrations of ionic liquids for the chromatographic procedure were 0.1 mM in aqueous solution. The structure and main properties of ILs studied are listed in Table 1. Hydrophobicity of cations expressed as log P values was calculated with HyperChem software.

The mobile phase contained acetonitrile and methanesulfonic acid for ion chromatography (Fluka, Buchs, Switzerland). The pH of the methanesulfonic acid was measured before mixing with the organic modifier. Isocratic and gradient grade acetonitrile were used as obtained from J.T. Baker (J.T. Baker, Deventer, The Netherlands). The potassium hydroxide was obtained from POCh (POCh, Gliwice, Poland).

Chromatographic Procedure

The IL cations were analyzed at a flow rate of 1 mL min^{-1} under isocratic conditions. The injected sample volume was 20 µL. During chromatographic investigations, the columns were thermostated at 35°C and suppressor with conductometric detector at 30°C. The micromembrane suppressor was regenerated using 40 mM KOH delivered at approximately the flow rate of 7 mL min^{-1}. The mobile phase composition of acetonitrile with methanesulfonic acid of five different concentrations of MSA varied from 1 to 9 mM and the concentration of acetonitrile varying from 20 to 75% (v/v), was used at isocratic conditions.

Retention factors k were calculated as $k = V_R / V_M - 1$, where V_R is retention volume and V_M is the hold-up volume measured by the system peak of mobile phase.

The graphs for the results interpretation were plotted using OriginPro program v. 7 (OriginLab Corporation, MA, USA). In the interpretation of the results the HyperChem v.5.1 package with the ChemPlus extension (HyperCube, Waterloo, Canada) was also used.

RESULTS AND DISCUSSION

Imidazolium and pyridinium ionic liquid cations were chosen for investigation, because they are the most commonly used in organic synthesis, catalysis, and other analytical fields.[4–8] Therefore, methods for their quantitative and qualitative analysis are of great need.

Influence of Acetonitrile on the Retention of Cations

Packings used in IC are usually bifunctional, with the organic ligand supporting the ion exchange group, bonded to the support surface. In the case of the present study, packing material consists of crown ether, carboxylate and phosphonate groups bonded to polymeric support of ethylvinylbenzene crosslinked with divinylbenzene. This packing material is of medium cation exchange strength. When non polar solutes are analyzed by IC, the hydrophobic amount of the ligand may influence the retention of those compounds. As a consequence, the retention will follow the reversed phase mechanism. To avoid this effect, organic modifier may be used as a mobile phase component. For this purpose, acetonitrile (ACN) was utilized. In Figure 1 obtained results were presented as the dependencies of k vs. acetonitrile amount (φ) in mobile phase for different methanesulfonic acid (MSA) concentrations. The Soczewinski-Snyder type linear relationship was utilized for the estimation of molecular interactions in the chromatographic system:

$$\log k = \log kw - S\varphi \qquad (1)$$

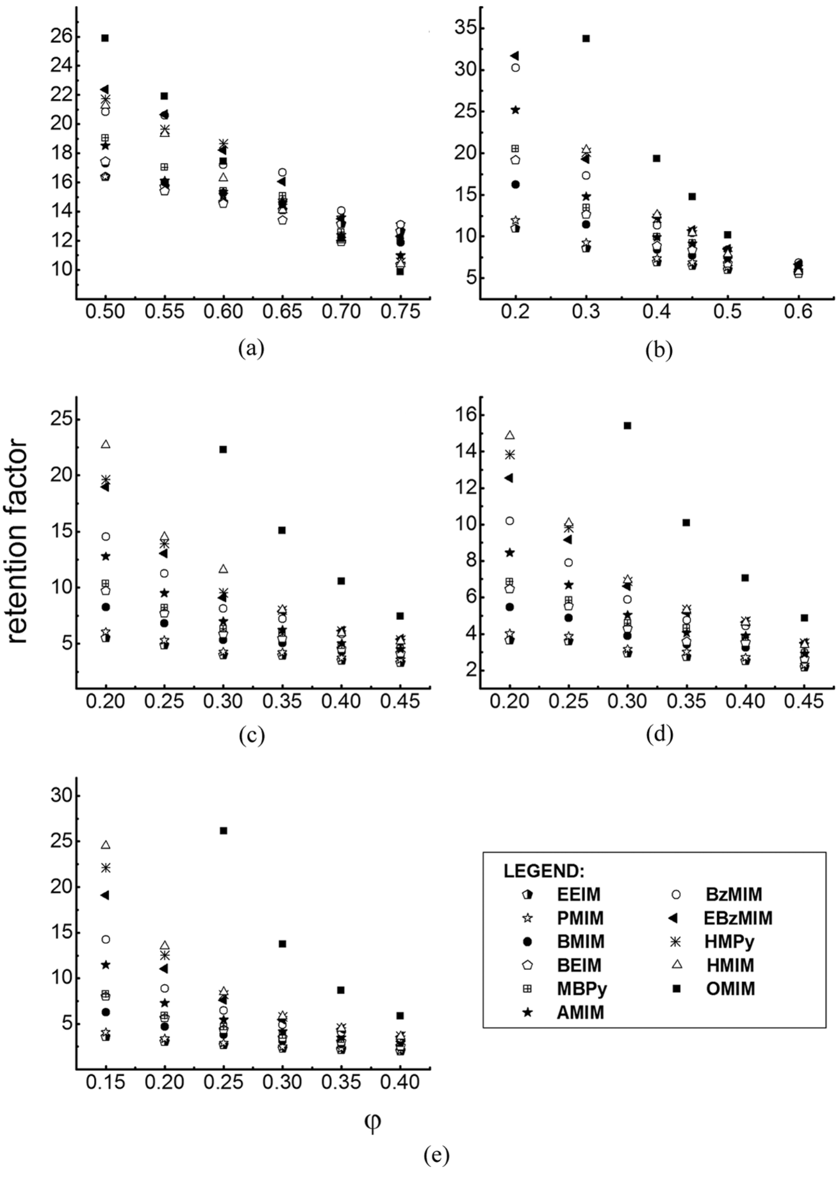


FIGURE 1 Influence of acetonitrile amount in the mobile phase on retention factors of the 1,3-dialkylimidazolium, 1-aryl-3-methylimidazolium and pyridinium cations for several methanesulfonic acid concentration: a) 1 mM, b) 2.5 mM, c) 5 mM, d) 7.5 mM, e) 9 mM.

Retention factor values are reduced with the increase of the ACN content for each cation and MSA concentration. In the case of 2.5, 5, 7.5, and 9 mM of MSA (Figures 1b–e) graphs are similar, the exception concerns the very low concentration of MSA (Figure 1a) for which changes in elution order were observed. For the homologous series of 1,3-dialkylimidazolium ionic liquids (EEIM, PMIM, BMIM, BEIM, AMIM, HMIM, OMIM), when 50% v/v of ACN flows through the column, the highest retention has the most hydrophobic OMIM cation (Table 1). Beyond 60% v/v of ACN the elution order follows the hydrophobicity of studied cations: OMIM> HMIM>AMIM>BEIM>BMIM>PMIM>EEIM (Table 1, Figure 1a). Such effect is typical for reversed phase HPLC and indicates that retention mechanism of imidazolium cations is mainly based on hydrophobic side, alkyl chain interactions. The addition of the organic modifier results in a distinct reduction in the retention times of all solutes, but also inverts the order of elution. At concentrations of ACN higher than 65% v/v hydrophilic EEIM elutes after OMIM (Figure 1a). Polar cations of low molecular masses are than strongly retained in the column and elution follows the normal phase pattern (Table 1, Figure 1a). The predominant role in retention mechanism will play cation exchange chromatography (on phosphonium and carboxylic groups) within the high concentration range of added organic modifier. A similar situation for 1 mM of MSA was observed in the case of 1-alkyl-3-arylimidazolium (BzMIM and EBzMIM) and pyridinium cations (MBPy, HMPy). The changes in *k* exhibit the same pattern as those of the 1,3-dialkylimidazolium ionic liquids. The *k* values were greater for EBzMIM and HMPy at ACN concentration lower than 60% v/v, otherwise retention for those cations was of low values

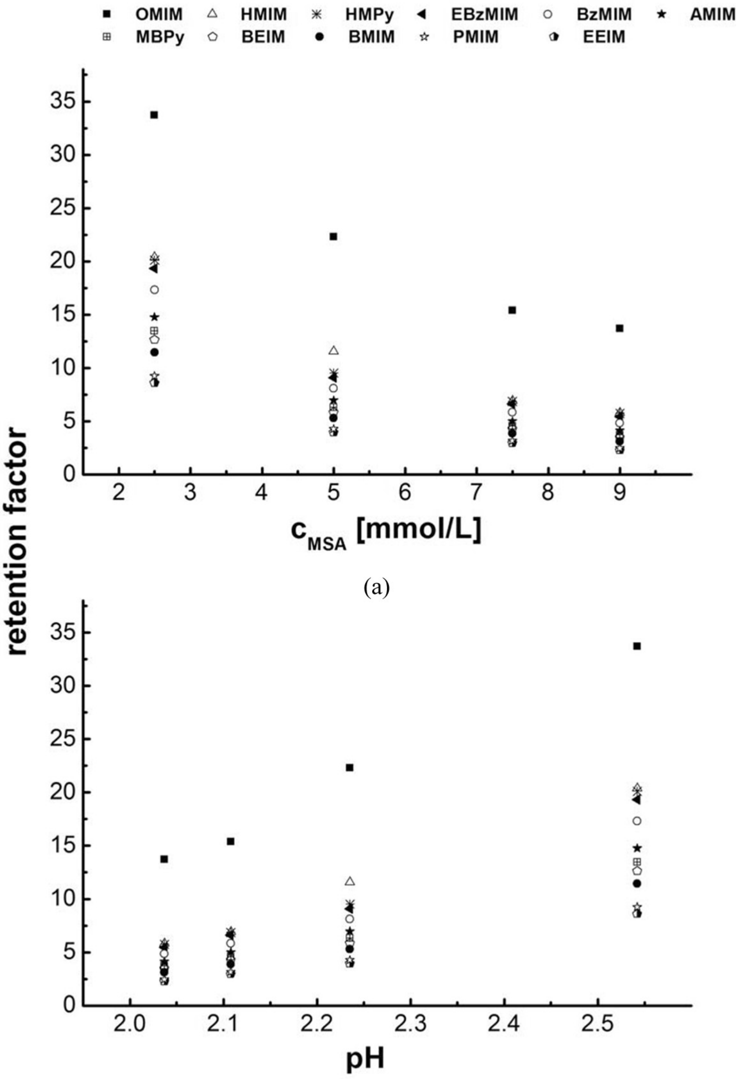
Dependencies presented in Figures 1b, c, d, and e show simple tendencies of decreasing *k* values for higher ACN over the whole investigated organic modifier range. However, studies were performed for different ACN concentration in mobile phase: from 15 to 40% v/v, than in case of 1 mM of MSA (Figure 1a). As higher concentrations of acetonitrile cause the cations elution at the dead volume and lower concentrations reflect in long analysis time, tests were performed only within this range. The differences in retention values become slender over 40% v/v of organic solvent. There is a clear reversed phase order of elution in the case of homologous series of 1,3-alkylimidazolium cations with side chains length varying from ethyl to octyl. The hydrophobic interactions occur probably between alkyl groups localized in cations structure and crown ether groups, which are present at the packing surface. They seem to be the most influential in the retention mechanism. On the other hand *k* values in some cases have similar values for ionic liquid cations of different hydrophobicity (Table 1, Figure 1). Such effect concerns ions of different structure properties like imidazolium BEIM and pyridinium MBPy, but also for 1,3-dialkylimidazolium HMIM, 1-aryl-3-methylimidazolium EBzMIM and pyridinium HMPy. Log P value for HMIM equals 1.47, while for HMPy 2.47, nevertheless both ions are retained in the column showing similar time (Table 1, Figure 1). The same situation relates to BEIM and MBPy, and also to OMIM, which interact with the packing surface in the strongest way (the highest k values), while HMPy appeared to have the greater log P (Table 1, Figure 1). Probably competition for ionized phosphonium and carboxylic groups determines the chromatographic behavior of these cations in greater matter in comparison with cations from homologous series. Except for electrostatic attraction between ionized groups on packing material and analyzed cations, the other reason of the discussed effect is also possible, namely the log P calculation method. Hydrophobicity expressed as log P value is the most common measure of compound polarity and relates to amountition of the substance between n-octanol and water. However, the optimal method for experimental determination of log P for ionic liquids was not developed yet, therefore hydrophobicity is calculated with many programs and calculation methods. We have used HyperChem software. The main drawback of calculations performed with this program is omission of charge localized in the cations.

Influence of Acid Concentration on the Retention Factor Values

Buffer concentration and pH are two parameters, which are carefully controlled in IC. The eluting strength and selectivity are determined by the competing counter ion, therefore the proper choice of buffer salt or acid is of a great matter. In the present study, several different MSA concentrations were investigated for a few various acetonitrile amounts in mobile phase. The influence of buffer concentration on retention factors was examined for all the ionic liquids in the range from 1 to 9 mM of methanesulfonic acid in 30% (v/v) acetonitrile in mobile phase. However, tendencies presented for this mobile composition are analogous for all other compositions investigated in the study. The results, plotted as a *k* vs. acid concentration are shown in Figure 2a. For each cation with the increase of MSA concentration *k* values were reduced. This effect is typical for IC and was expected. By increasing the salt concentration, the molecules of weakest ionic interactions with functional groups on the packing are disrupted first and eluted earlier. Solutes that have a very strong ionic interaction require higher salt concentration to disrupt bonds between them and the packing surface.

Obtained results allowed for choosing the preliminary conditions for the separation of eleven ionic liquid cations mixture. Results presented in Figure 2a indicate that the greatest differences of *k* between analyzed ions were obtained for 1 mM of MSA, however, analysis times were very long. For that reason 2.5 mM of acid was applied in the initial separation of pyridinium and imidazolium cations.

Although a wide range of acid concentration was used, separation of several cations remained insufficient (similar retention factor values).



(a)

(b)

FIGURE 2 Influence of methanesulfonic acid concentration (mM) on the retention factors of imidazolium and pyridinium ionic liquid cations for 30% v/v of acetonitrile in mobile phase.

This effect concerns especially HMIM, HMPy, EBzMIM over almost the whole MSA concentration range. The same applies to two other pairs of cations: AMIM and BzMIM, BEIM and MBPy in 7.5 and 9.0 mM of MSA. All of those cations differ in hydrophobicity (Table 1), therefore, similar retention cannot be connected with their polarity. The effect of acid concentration is probably related with competition between ionic liquid cations for active ion exchange sites on the support surface.

Influence of Ph of Mobile Phase on Ionic Liquid Retention

In the case of our study, the effect of pH on retention of ionic liquid cations is strictly connected with the MSA concentration. In Figure 2b, relationships between imidazolium cation and mobile phase pH were presented. The increase of pH causes greater *k* values. High pH results in ionization of carboxylate and phosphonate groups on the polymeric resin surface. As a consequence, electrostatic attraction between solute and those groups is stronger and retention higher. Changes in selectivity are analogous as in the case of alterations made in MSA concentration. The application of pH equal to 2.54 (2.5 mM of MSA) assures significant differences in *k* values for studied cations.

Separation of Ionic Liquid Cations in Isocratic Elution Conditions

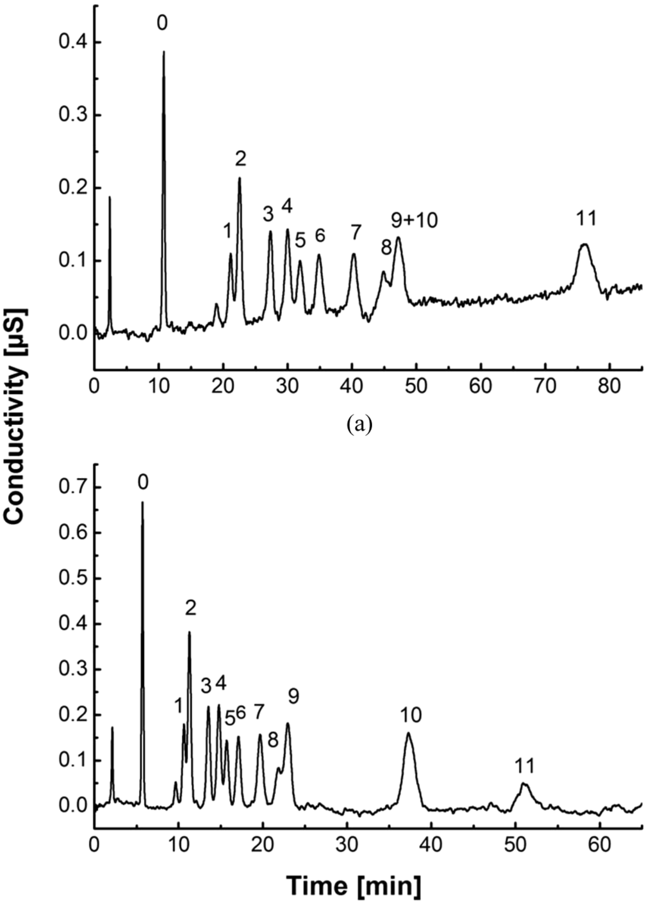
Resolution of compounds analyzed with the use of IC is influenced by pH of mobile phase and ionic strength of buffer or acid. Therefore, when the optimal amount of ACN in mobile phase for the separation of studied cations was chosen, we have focused on the choice of MSA concentration and pH. The high ACN percent in the mobile phase caused elution of analyzed compounds in the dead volume of the column, especially with the use of high concentrations of MSA. On the other hand, low a ACN amount resulted in long analysis times and, as a consequence, HMPy, HMIM, and OMIM were not detected because of peaks bordering. For these reasons, separation was unsuccessful with 30% of ACN and 2.5 or/and 5 mM MSA. Although separation of eleven ionic liquid cations was tested for all five

TABLE 2 Separation Parameters Determined for Isocratic Elution Conditions: Retention Factor (*k*), Selectivity (α), Resolution (R_s), and Asymmetry Factor (f_{AS}), Appointed at 10% of Peak Height

Ionic Liquid Cation	30% v/v ACN, 70% v/v 2.5 mM MSA				30% v/v ACN, 70% v/v 5 mM MSA			
	k	f_{AS}	α	R_s	*k*	f_{AS}	α	R_s
EEIM	8.594	—			3.970	—		—
PMIM	9.264	—	1.08	1.31	4.276	—	1.08	
BMIM	11.444	0.95	1.24	3.66	5.312	0.94	1.24	2.98
BEIM	12.660	—	1.11	1.77	5.876	—	1.11	1.46
MBPy	13.460	—	1.06	1.25	6.317	—	1.08	1.02
AMIM	14.776	0.87	1.09	1.87	6.964	1.00	1.10	1.46
BzMIM	17.327	0.83	1.17	2.97	8.126	1.14	1.16	2.32
EBzMIM	19.318	—	1.11	2.41	9.101	—	1.12	2.11
HMPy	20.105	—	1.04	1.09	9.529	—	1.05	1.03
HMIM	20.379	—	1.01		11.555	1.14	1.21	7.48
OMIM	33.718	0.94	1.65	10.19	22.299	1.05	1.93	5.27

MSA concentrations, only two results were presented in this study. Estimation of the final separation result was done on the basis of comparison of some characteristic retention parameters listed in Table 2. Chromatograms are presented in Figure 3.

Chromatograms presented in Figure 3 are marked by appearance of the unknown substance signal (first peak, noticed in Figure 3 as 0). This peak appeared in all chromatograms of analyzed cations in the same time for similar experimental conditions. The most probable explanation of this phenomenon is its origin. It derives from impurities after the ionic liquids



(b)

FIGURE 3 Chromatograms of separation of ionic liquid cations mixture with isocratic elution for mobile phase consisting of 30% v/v of acetonitrile and: a) 70% v/v of 2.5 mM MSA, b) 70% v/v of 5 mM MSA. Key: 0 – unknown compound, 1 – EEIM, 2 – PMIM, 3 – BMIM, 4 – BEIM, 5 – MBPy, 6 – AMIM, 7 – BzMIM, 8 – EBzMIM, 9 – HMPy, 10 – HMIM, 11 – OMIM.

synthesis process –1-methylimidazolium. This observation proves the applicability of IC for determination of ionic liquid purity.

Separation of all studied cations for 2.5 mM of MSA was shown in Figure 3a. The analysis time was long and equals 80 minutes. The resolution of EEIM and PMIM, BEIM and MBPy was insufficient, because R_s values are between 1.25 and 1.31 (Table 2), while HMPy and HMIM were not separated. In the case of 5 mM selectivity and resolution for EEIM and PMIM, BEIM and MBPy was not improved (Table 2). However the total time for the separation of cations was shorter than for 2.5 mM and R_s for HMIM and HMPy equals 7.48 (Figure 3b, Table 2).

Application of ion chromatography allows separation of ionic liquid cations, however, when imidazolium and pyridinium compounds are analyzed in a mixture, resolution is not sufficient. The reason of poor resolution and selectivity for those two types of ionic liquid cations is connected with specific interactions, which occur during the chromatographic process.

CONCLUSION

The ionic nature of studied substances makes ion chromatography an interesting analytical tool for their analysis. Application of cation exchange packing material in the study of imidazolium and pyridinium ionic liquid cations allows investigation of their chromatographic behavior as a function of several parameters. The first one is the concentration and pH of methanesulfonic acid in mobile phase. It was proven that with the increase of concentration and decrease of pH the retention factors were reduced. When the influence of the ACN amount in mobile phase was investigated, some interesting trend was observed for low MSA concentration. Between 2.5 and 9 mM of MSA the elution order of ionic liquid cations follows reversed phase order, where the hydrophobicity is the most influential parameter. On the other hand, 1 mM of MSA leads to two different retention mechanisms depending on the ACN amount in mobile phase. When ACN contribution is less than 60% v/v – ionic liquid retention depends on hydrophobic properties, while when amount of ACN increase up to 75% v/v, then retention of cations follows normal phase order. Comparison of retention factors between three groups of ionic liquid types: 1,3-dialkylimidazolium, 1-aryl-3-alkylimidazolium and pyridinium indicate the main type of interaction in retention mechanism is electrostatic attraction. Investigated cations were separated with cation exchange resin, however the resolution between some of cations was insufficient. Application of this method would lead to improvement in resolution if the mixture consists just of imidazolium or just of pyridinium cations.

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