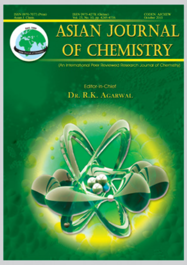
Asian Journal of Chemistry; Vol. 24, No. 2 (2012), 601-606

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Effect of Ionic Liquids Additive on the Retention Factor of Different Kinds of Compounds

H.J. HEO, D. HAN and K.H. ROW*

Department of Chemical Engineering, Inha University, Incheon 402-751, South Korea

*Corresponding author: Fax: +82 32 8720959; Tel: +82 32 8607470; E-mail: rowkho@inha.ac.kr

(*Received*: 27 January 2011; *Accepted*: 10 October 2011) AJC-10489

Ionic liquids can be used as mobile phase additives in reversed-phase liquid chromatography (HPLC) when mixed with other solvents such as methanol and acetonitrile. The addition of ionic liquids can alter analytes' retention factors decrease band tailing, reduce band broadening and improve resolution partly because of the competition between imidazolium cations and the analyte's polar groups for the silanol group on the alkyl silica surface along with the formation of weak bilayer electronic structures on the C_{18} column. Five ionic liquids were used and their influences on the retention factors of different compounds were studied. Elution profiles were calculated by plate theory based on linear and quadratic equations of retention factor, $\ln k = \ln k_w + SC$, $\ln k = L + MC + NC^2$, where C is the concentration of ionic liquid. The results show that all the five ionic liquids greatly affected basic compounds.

Key Words: Ionic liquids, Mobile phase, Retention factor, Snyder equation, Binary-polynomial equation.

INTRODUCTION

Ionic liquids (ILs), known as melt salts[1], have properties suitable for many area of analytical chemistry. They have recently been used to facilitate the use of less polluting solvents and are increasingly being tested as reaction media[2-6].

Ionic liquids are normally composed of relatively large organic cations and inorganic or organic anions. Their control of coupling in chemical reactions gives them much industrial potential. Unlike molecular liquids, ionic liquids, which are polar solvents, have less environmental impact, are non-volatile and nonflammable. Most of them are soluble in water and stable in air[7]. They have therefore been dubbed 'green solvents'[8,9]. Ionic liquids can be used in syntheses because they can control compounds' physical properties, melting points, viscosities, densities, hydrophilicities and hydrophobicities through the choice of cation and anion, earning them the epithet 'designer solvents'[10,11].

Ionic liquids have recently been used as additives in the mobile phase of RP-HPLC[12,13]. Their chemical nature suggests that when they are added to the mobile-phase of HPLC, they are present in solution in the mobile phase and also coat the reversed-phase silica-based columns. ionic liquids as mobile-phase additives could play many roles, for example blocking residual silanol groups, modifying the stationary phase or acting as ion-pairing agents[14].

Retention factors can be investigated through many practical retention models, such as the linear salvation energy relationships (LSER) model, which have been widely used for the prediction and interpretation of retention processes. Furthermore, some properties such as ln k (k is the retention factor) can be related to fundamental molecular characteristics of the solvents and solutes involved in physico-chemical processes[15,16].

In this study, five ionic liquids were used to investigate the retention factors of different compounds, basic and acidic. Retention factors were calculated from plate theory based on linear and quadratic equations of retention factor, $\ln k = \ln k_w + SC$, $\ln k = L + MC + NC^2$, where C is the concentration of ionic liquids. They were used to analyze the influence of the different ionic liquids on the retention factors of the different compounds.

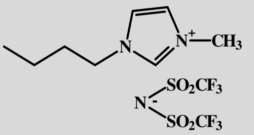
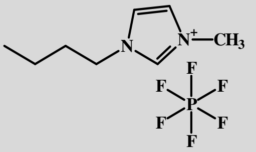
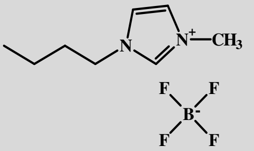
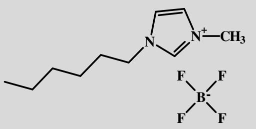
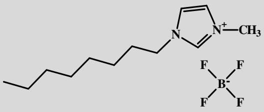
EXPERIMENTAL

Acetonitrile (HPLC grade, 99.5 %) and methanol (HPLC grade, 99.9 %) and aniline (extra pure grade, 99.9 %) were obtained from Duksan Pure Chemical Co., Ltd. (Korea). Caffeine (99.5 %), pyridine (99.5 %) and phenol (99.5 %) were obtained from Sigma-Aldrich (USA). *p*-Cresol (extra pure grade, 99.9 %) was bought from Junsei Chemical Co., Ltd (Japan). 2-Anilinoethanol (98.5 %) and *p*-toluidine (99 %) and 2-chloroaniline (98 %) were purchased from Tokyo Chemical Industry Co., Ltd (Japan).

Ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate (98 %) and 1-butyl-3-methylimidazolium hexafluorophosphate (98 %) were purchased from C-TRI (Korea), 1-hexyl-

3-methylimidazolium tetrafluoroborate and 1-octyl-3-methylimidazolium tetrafluoroborate (98 %) 1-butyl-3-methyl imidazolium *bis*(trifluoromethylsulfonyl)imide were bought from Sigma-Aldrich (USA). The chemical structure of ionic liquids with their respective molecular weight are given in Table-1.

TABLE-1
CHEMICAL STRUCTURES OF IONIC LIQUIDS

No.	Name	Abbr.	Structure
1	1-Butyl-3-methyl imidazolium *bis*(trifluoromethyl-sulfonyl)imide (m.w. = 284.18)	[Bmim][Tf_2N]	
2	1-Butyl-3-methylimidazolium hexafluorophosphate (m.w. = 226.03)	[Bmim][PF_6]	
3	1-Butyl-3-methylimidazolium tetrafluoroborate (m.w. = 226.03)	[Bmim][BF_4]	
4	1-Hexyl-3-methylimidazolium tetrafluoroborate (m.w. = 254.08)	[Hmim][BF_4]	
5	1-Octyl-3-methylimidazolium tetrafluoroborate (m.w. = 282.13)	[Omim][BF_4]	

Preparation of mobile phase and samples: In the first part, the retention times of the five solutes were compared according to the amount of ionic liquid additive (0, 5, 10, 15 and 20 mM) in the mobile phase (acetonitrile/water, 30/70, v/v %). The second part involved changing the mobile phase to methanol/water, 40/60, v/v % and using ionic liquids additive at concentrations of 0, 1, 3, 5, 10, 15, 30 mM.

Five solutes were used in each experiment: The first employed caffeine, pyridine, aniline, phenol and *p*-cresol diluted to 1 mg/mL in acetonitrile and the second employed pyridine, aniline, 2-anilinoethanol, *p*-toluidine and 2-chloro-aniline diluted to 1 mg/mL in methanol.

Analytical condition of HPLC: Chromatography was performed with a Waters 600 s multisolvent delivery system, a Waters 616 liquid chromatography and a Waters 2487 variable wavelength, dual-channel, UV detector (Waters Associates, Milford, MA, USA). A six-port Rheodyne injector (20 µL sample loop) was also used. Data processing was performed with Millennium 3.2 software resident in an HP Vectra 500PC. Compounds were separated on a 150 mm × 4.6 mm, 5 µm particle, OptimaPak C18 column (RS Tech, Daejeon, Korea). The wavelength of the detector was fixed at 254 nm (mobile phase acetonitrile 30 %) or 240 nm (mobile phase methanol 40 %) with a flow rate of 0.5 mL/min and injection volume of 5 µL.

RESULTS AND DISCUSSION

Retention factor and Snyder, binary-polynomial equation: The concentration 0 mM indicates a mobile phase (acetonitrile/water = 30/70) without any ionic liquids. The k value was calculated using the following equation (1).

$$k = (t_R - t_0)/t_0 \qquad (1)$$

where t_R is the retention time of the target compound and t_0 is the dead time. In this experiment, the dead time was obtained using KNO_3 as a marker. Elution information calculated by plate theory based on the linear (2) and quadratic (3) equations of retention factor was used to investigate correlations between the retention factors

$$\ln k = \ln k_w + SC \qquad (2)$$

$$\ln k = L + MC + NC^2 \qquad (3)$$

where S, L, M, N, ln (k_w) and S are empirical constants, which should be experimentally determined. Equations (2) and (3) were applied to the mobile phase in RP-HPLC[16,17].

In this study, the Snyder (2) and binary polynomial (3) equations were used to investigate the relationship of five materials' retention factors according to the type and composition of the ionic liquid. Ionic liquids were added to fixed compositions of the organic solvent. C was substituted as the concentration of ionic liquid instead of the concentration of the organic solvent as the variable in the above two equations.

Application of Snyder and binary-polynomial equations: Caffeine, pyridine, aniline, phenol and *p*-cresol were tested to investigate the influence of ionic liquids on retention time (Table-2). [Bmim][Tf_2N] and [Bmim][PF_6] are two common hydrophobic ionic liquids. When they were added to the mobile phase, the retention factor of the five compounds almost all decreased compared with the retention factor without ionic liquid. Increasing the concentration of these ionic liquids further decreased the retention factors.

The retention factors of pyridine and aniline changed more than those of the other three compounds, especially when hydrophilic ionic liquids [Bmim][BF_4], [Hmim][BF_4], [Omim][BF_4] were added to the mobile phase. The retention factors of pyridine and aniline decreased with increasing concentrations of ionic liquid, while the retention factors of caffeine, phenol and *p*-cresol were almost constant with increasing concentrations of ionic liquid. The results show that the addition of ionic liquid has a larger effect on basic compounds.

In order to describe better influence of ionic liquids on the retention factor, the Snyder equation (2) and binary polynomial equation (3) were applied. The constants, k_w, S, L, M, N and r^2 are shown in Tables 3 and 4. The retention parameters of ionic liquid obtained at the isocratic elution mode were investigated. The linear regression of the logarithm of the retention factor of the analytes, ln k, against the concentration of the ionic liquid in the mobile phase, C, was used for the chromatographic determination of ln k_w (eqn. 2). The k_w is the intercept corresponding to k in pure water or aqueous buffer as the mobile phase, S is a constant for a given analyte or

TABLE-2
RETENTION FACTOR OF FIVE SOLUTES WITH DIFFERENT CONCENTRATION OF IONIC LIQUIDS

Ionic liquid	Conc. (mM/L)	Retention factor k				
		Caffeine	Pyridine	Aniline	Phenol	*p*-Cresol
$[Bmim][Tf_2N]$	0	0.6598	1.3556	3.3609	3.9135	6.6799
	5	0.6145	1.3862	3.1778	3.6299	6.4894
	10	0.5899	1.3589	3.1412	3.5240	6.2165
	15	0.5952	1.2870	3.1379	3.4741	6.0514
	20	0.5912	1.1738	3.1505	3.3629	5.8822
$[Bmim][PF_6]$	0	0.6598	1.3556	3.3609	3.9135	6.6799
	5	0.6365	1.2304	3.2224	3.7777	6.6304
	10	0.6320	1.1576	3.1389	3.7461	6.6058
	15	0.6285	1.1032	3.0833	3.7211	6.5847
	20	0.6212	1.0473	2.9162	3.6146	6.4841
$[Bmim][BF_4]$	0	0.6598	1.3556	3.3609	3.9135	6.6799
	5	0.6498	0.5180	2.1691	3.8549	7.0374
	10	0.6565	0.4847	2.0906	3.7537	7.1586
	15	0.6691	0.4661	2.0047	3.7038	6.7538
	20	0.6745	0.4128	1.6332	3.8862	7.1905
$[Hmim][BF_4]$	0	0.6598	1.3556	3.3609	3.9135	6.6799
	5	0.6545	0.5633	2.9215	3.8017	6.8776
	10	0.6491	0.4927	2.8816	3.7910	6.8416
	15	0.6389	0.4422	2.8076	3.7705	6.7773
	20	0.6332	0.4274	2.7118	3.7517	6.7478
$[Omim][BF_4]$	0	0.6598	1.3556	3.3609	3.9135	6.6799
	5	0.6405	0.5526	2.6871	3.7697	6.6612
	10	0.6358	0.5273	2.5353	3.7431	6.6213
	15	0.5984	0.5160	2.4750	3.6804	6.5911
	20	0.5866	0.5033	2.4514	3.6692	6.5474

TABLE-3
PARAMETERS OF SNYDER EQUATION USING DIFFERENT CONCENTRATION OF IONIC LIQUIDS

Ionic liquids	Target compound	$\ln k = \ln k_w + SC$		r^2
		k_w	S	
$[Bmim][Tf_2N]$	Caffeine	0.6410	-0.0052	0.7191
	Pyridine	1.4083	-0.0072	0.7258
	Aniline	3.2845	-0.0028	0.5924
	Phenol	3.8331	-0.0069	0.9142
	p-Cresol	6.6765	-0.0065	0.9934
$[Bmim][PF_6]$	Caffeine	0.6527	-0.0027	0.8530
	Pyridine	1.3304	-0.0125	0.9773
	Aniline	3.3538	-0.0066	0.9698
	Phenol	3.8862	-0.0035	0.9218
	p-Cresol	6.6848	-0.0013	0.9121
$[Bmim][BF_4]$	Caffeine	0.6523	0.0015	0.6038
	Pyridine	0.9527	-0.0497	0.6639
	Aniline	2.9637	-0.0304	0.8288
	Phenol	3.8629	-0.0108	0.1310
	p-Cresol	6.8144	0.0021	0.2473
$[Hmim][BF_4]$	Caffeine	0.6610	-0.0021	0.9841
	Pyridine	0.9815	-0.0510	0.7120
	Aniline	3.2165	-0.0094	0.8170
	Phenol	3.8763	-0.0019	0.7898
	p-Cresol	6.7770	0.0001	0.0057
$[Omim][BF_4]$	Caffeine	0.6626	-0.0061	0.9457
	Pyridine	3.8706	-0.0031	0.8750
	Aniline	3.0939	-0.0143	0.7415
	Phenol	3.8706	-0.0031	0.8750
	p-Cresol	6.6874	-0.0010	0.9854

TABLE-4
PARAMETERS OF BINARY-POLYNOMIAL EQUATION USING DIFFERENT CONCENTRATION OF IONIC LIQUIDS

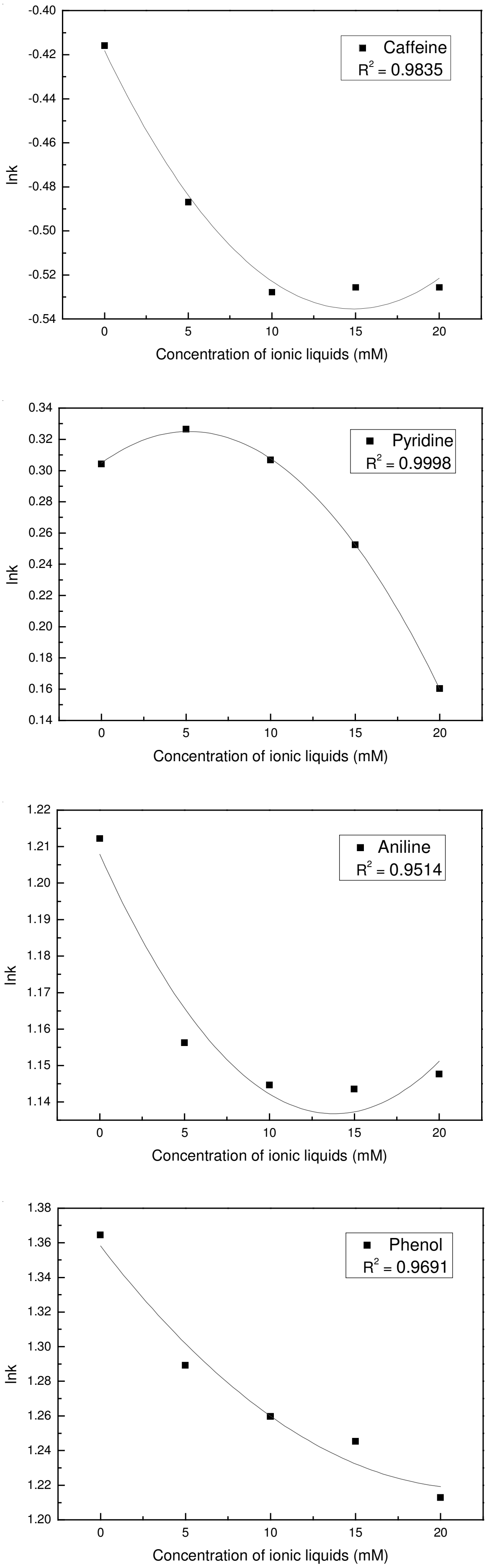
Ionic liquids	Target compound	$\ln k = L + MC + NC^2$			r^2
		L	M	N	
$[Bmim][Tf_2N]$	Caffeine	-0.4182	-0.0158	0.00053	0.9835
	Pyridine	0.3048	0.0078	-0.00075	0.9998
	Aniline	1.2079	-0.0103	0.00037	0.9514
	Phenol	1.3581	-0.0013	0.00029	0.9691
	p-Cresol	1.9010	-0.0075	0.00005	0.9954
$[Bmim][PF_6]$	Caffeine	-0.4196	-0.0055	0.00014	0.9390
	Pyridine	0.3001	-0.0184	0.00029	0.9960
	Aniline	1.2074	-0.0055	0.00005	0.9721
	Phenol	1.3695	-0.0043	0.00004	0.9262
	p-Cresol	1.8977	-0.0005	-0.00004	0.9462
$[Bmim][BF_4]$	Caffeine	-0.4194	-0.0017	0.00016	0.8493
	Pyridine	0.1956	-0.1473	0.00488	0.8882
	Aniline	1.1522	-0.0568	0.00132	0.8830
	Phenol	1.3713	-0.0091	0.00040	0.7576
	p-Cresol	1.9113	0.0052	-0.00015	0.2931
$[Hmim][BF_4]$	Caffeine	-0.4154	-0.0016	-0.00003	0.9896
	Pyridine	0.2262	-0.1490	0.00490	0.9416
	Aniline	1.1967	-0.0207	0.00057	0.9216
	Phenol	1.3614	-0.0045	0.00013	0.9254
	p-Cresol	1.9034	0.0042	-0.00020	0.6926
$[Omim][BF_4]$	Caffeine	-0.4164	-0.0041	-0.00010	0.9541
	Pyridine	0.2075	-0.1422	0.00506	0.8872
	Aniline	1.1955	-0.0407	0.00132	0.9642
	Phenol	1.3619	-0.0064	0.00017	0.9681
	p-Cresol	1.8993	-0.0007	-0.00002	0.9959

congeneric group of analytes and C is the concentration of ionic liquid in the eluent. And L, M and N are regression coefficients with characteristic values for a given solute and column-solvent system (eqn. 3)[18,19].

The constants k_w and L from the Snyder equation and the binary polynomial equation had a large effect on the quadratic equation. Other constant, S, M, N had a small effect on the equation because of their low magnitudes. The elution order of the five compounds was caffeine, pyridine, aniline, phenol, *p*-cresol. The regression coefficients were very low regardless of ionic liquid, implying that this equation has difficulty reflecting the effect of ionic liquid on retention factor. The regression coefficients, r^2, of all the five compounds approached 1.00 in eqn. 3.

The retention factors of the five compounds calculated by the binary-poly equation approached 1.0 and showed closer agreement with the experimental data than the Snyder equation. In this work, the binary-poly equation was used to describe the effect of ionic liquids. Fig. 1 shows binary-poly curves of the retention factor according to the concentration of $[Bmim][Tf_2N]$.

Effect of ionic liquids on the basic compounds: The addition of ionic liquids was found to have a larger effect on basic compounds, so three compounds (2-anilinoethanol, *p*-toluidine, 2-chloroaniline) with structures similar to pyridine and aniline were investigated with ionic liquids. Retention factors, k, were calculated using eqn. 1 for varying concentrations of ionic liquids (Table-5). The influence of varying concentrations of different ionic liquids is shown in Fig. 2(a-e).



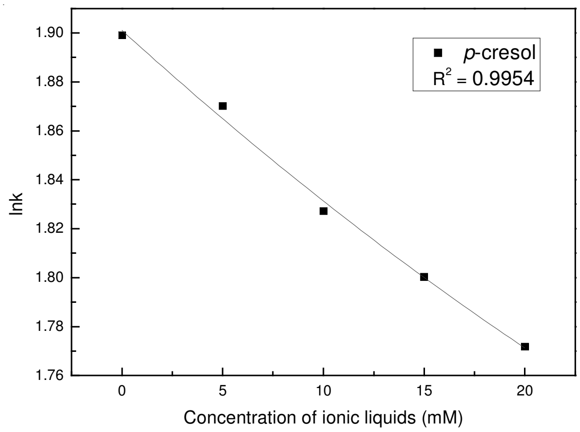
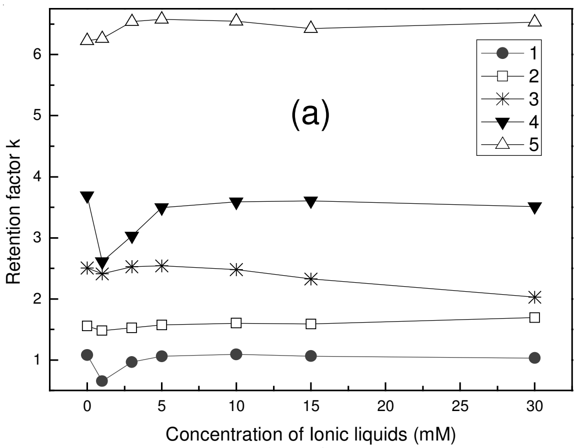


Fig. 1. Binary-polynomial curve of influence of [Bmim][Tf_2N] on the retention factors of five solutes

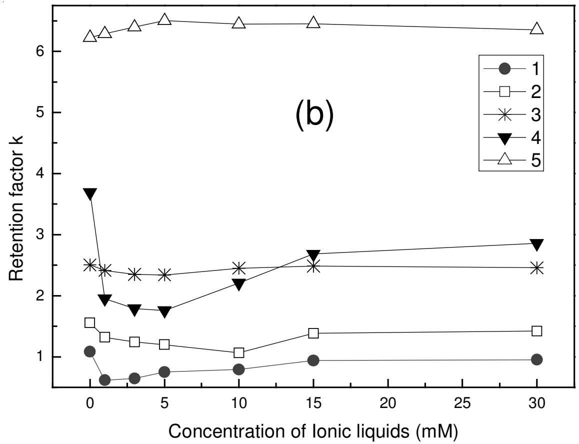
TABLE-5
RETENTION FACTOR OF FIVE SOLUTES WITH DIFFERENT CONCENTRATION OF IONIC LIQUIDS

Ionic liquid	Conc. (mM/L)	Retention factor k				
		A	B	C	D	E
[Bmim][Tf_2N]	0	1.0837	1.5558	2.5050	3.6895	6.2264
	1	0.9244	1.4787	2.4109	2.6089	6.2643
	3	0.9672	1.5257	2.5257	3.0315	6.5397
	5	1.0590	1.5720	2.5405	3.4951	6.5779
	10	1.0936	1.6013	2.4798	3.5869	6.5478
	15	1.0639	1.5887	2.3263	3.6081	6.4258
	30	1.0315	1.6940	2.0275	3.5135	6.5325
[Bmim][PF_6]	0	1.0837	1.5558	2.5050	3.6895	6.2264
	1	0.6152	1.3173	2.4123	1.9510	6.2881
	3	0.6467	1.2404	2.3493	1.7862	6.3961
	5	0.7511	1.1985	2.3403	1.7579	6.5023
	10	0.7926	1.0630	2.4496	2.2044	6.4461
	15	0.9393	1.3835	2.4856	2.6810	6.4524
	30	0.9519	1.4222	2.4564	2.8574	6.3547
[Bmim][BF_4]	0	1.0837	1.5558	2.5050	3.6895	6.2264
	1	0.3569	1.3380	2.3133	2.2863	6.0775
	3	0.3128	1.2129	2.2273	1.9627	6.1279
	5	0.1985	1.2021	2.1233	1.8938	6.2174
	10	0.1557	1.0734	1.6823	1.1220	6.3052
	15	0.1193	0.7264	1.5068	0.8897	6.5203
	30	0.0311	0.5401	1.1566	0.5738	6.3750
[Hmim][BF_4]	0	1.0837	1.5558	2.5050	3.6895	6.2264
	1	0.8159	1.0347	2.4388	2.0887	6.6936
	3	0.7597	1.3695	2.5441	1.7692	6.8646
	5	0.4046	1.0864	2.1256	1.0806	6.9470
	10	0.4307	1.0783	2.2007	1.1845	6.7895
	15	0.4028	1.0356	2.1342	1.1206	6.7615
	30	0.1256	0.7264	2.0527	0.4591	6.9204
[Omim][BF_4]	0	1.0837	1.5558	2.5050	3.6895	6.2264
	1	0.8848	1.2228	2.4429	2.3046	6.4366
	3	0.6913	1.1283	2.3610	1.6602	6.5689
	5	0.5194	0.8735	2.1558	1.1103	6.7008
	10	0.5131	0.8178	2.3524	1.3052	7.0176
	15	0.4636	0.8735	2.1832	1.0572	7.4875
	30	0.0612	0.5167	1.8506	0.3996	8.7679

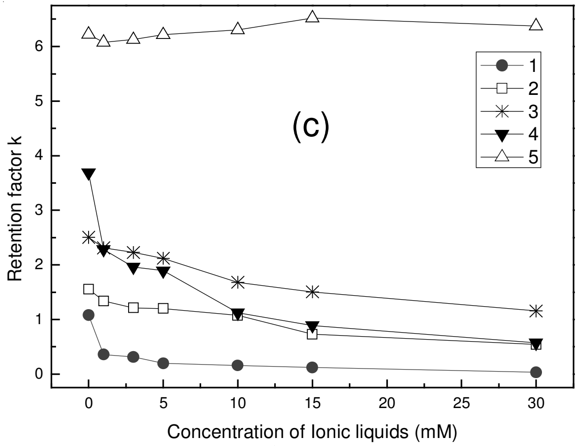
A = Pyridine, B = Aniline, C = 2-Anilinoethanol, D = *p*-Toluidine, E = 2-Chloroaniline.



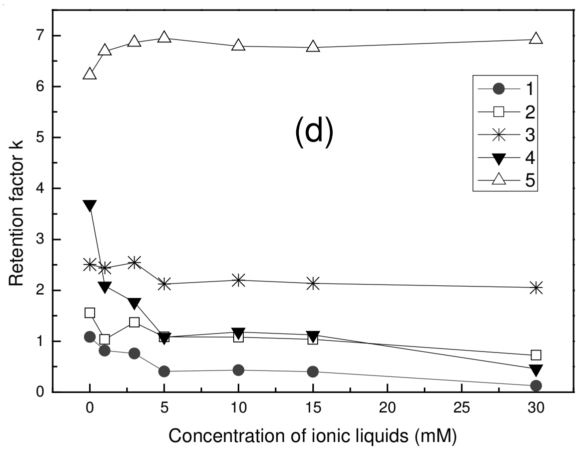
[Bmim][Tf_2N]



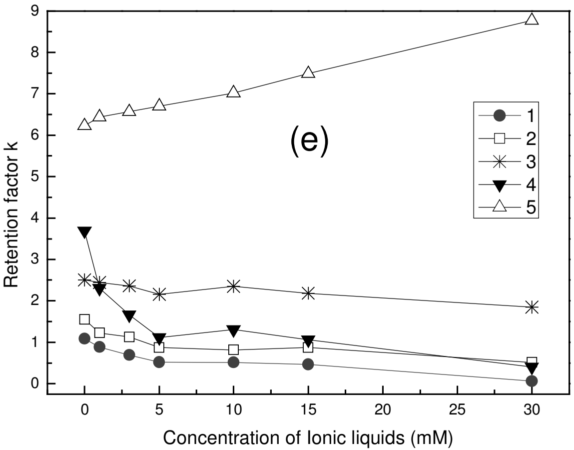
[Bmim][PF_6]



[Bmim][BF_4]



[Hmim][BF_4]



[Omim][BF_4]

Fig. 2. Influence of [Bmim]PF_6 on the retention factors of five solutes (1 = pyridine, 2 = aniline, 3 = 2-anilinoethanol, 4 = *p*-toluidine, 5 = 2-chloroaniline)

Fig. 2(a) and 2(b) show that increasing concentrations of the hydrophobic ionic liquids [Hmim][Tf_2N] and [Bmim][PF_6] caused retention factors of four solutes first decrease and then increase before leveling off. The retention factor of *p*-toluidine showed the largest change as it has a methyl group in the aniline structure that showed stronger interaction with ionic liquids than the other compounds. While, the retention factor of 2-chloroaniline first increased and then decreased. Retention factors of four solutes in the hydrophilic ionic liquids [Bmim][BF_4], [Hmim][BF_4] and [Omim][BF_4] first decreased and then leveled off with increasing concentration of ionic liquid. Fig. 2 shows that low concentrations of ionic liquids had the largest effect on pyridine. This was attributable to its strongly alkaline nature. [Bmim][BF_4], [Hmim][BF_4], [Omim][BF_4] have the same anion, with different cation alkyl chain lengths. The effect of the five solutes on retention factors significantly increased with increasing alkyl chain length, especially the retention factor of 2-chloroaniline, which increased more than the other compounds.

As salts ionic liquids have both cations and anions, with both species able to affect chromatographic results. Basic compounds most often bear positively charged amino groups in low pH mobile phases. Consequently these compounds are retained by a combination of electrical (charge-charge) and hydrophobic interactions with the stationary phase and the ions of the mobile phase. The mixed mechanism involves ion-pairing, ion-exchange and hydrophobic partitioning. Positions of basic compounds' peaks depend on the overall strength of the combined solute-stationary phase interactions in the aqueous mobile phase, charge interactions are usually stronger and slower than hydrophobic interactions. In this situation, $[Bmim]^+$ cations adsorbed on the C_{18} stationary phase without associating with the imipramine solute. The charges of the $[Bmim]^+$ covered stationary phase and repulsed those of imipramine. The retention factor was lower because of the faster hydrophobic interactions. The ionic liquid's ions adsorbed on the C_{18} surface and the chaotropic $[BF_4]^-$ anions associated with imipramine cations to form less polar ion pairs. Consequently, imipramine's retention factor increased and its peak shape improved because the fast hydrophobic interactions were mostly involved in the retention mechanism of the ion pair. The viscosity of the mobile phase increased with increasing concentration, which led to the increase of retention factors.

Conclusion

The addition of ionic liquid to the mobile phase had a large influence on compounds' retention factors, especially basic compounds, with results varying by ion type. A binary-poly equation was used to describe the influence of different concentrations of ionic liquids. The hydrophilic ionic liquid had larger effect on the retention factor of basic compounds. Therefore, ionic liquids can be used as mobile phase additive for the separation of basic compounds.

ACKNOWLEDGEMENTS

This research was supported by Basic Science Research Program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education, Science and Technology (2011-0010673).

REFERENCES

1. A. Berthod, M.J. Ruiz-Angel and S. Carda-Broch, *J. Chromatogr. A*, **1184**, 6 (2008).
2. M.J. Kim, M.Y. Choi, J.K. Lee and Y. Ahn, *J. Mol. Catalysis B: Enzymatic*, **26**, 115 (2003).
3. D.H. Zhang, S. Bai, M.Y. Ren and Y. Sun, *Food Chem.*, **109**, 72 (2008).
4. P. Siddharth, *Anal. Chim. Acta*, **556**, 38 (2006).
5. J. Liu, J. Åke Jönsson and G. Jiang, *TrAC-Trends Anal. Chem.*, **24**, 20 (2005).
6. Y. Polyakova, Y.M. Goo and K.H. Row, *Biotechnol. Bioprocess Eng.*, **11**, 1 (2006).
7. Y. Fan, M. Chen, C. Shentu and F. El-Sepai, *Anal. Chim. Acta*, **650**, 65 (2009).
8. J.D. Holbrey and K.R. Seddon, *Clean Prod. Process*, **1**, 223 (1999).
9. P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed. Engl.*, **39**, 3772 (2000).
10. H.Y. Ju, M.K. Lee and D.W. Park, *J. Korean Oil Chemists' Soc.*, **25**, 469 (2008).
11. M.H. Cho, H. Lee and H. Kim, *Korean Chem. Eng. Res.*, **48**, 1 (2010).
12. M.H. Abraham, J. Andonian-Haftvan, G.S. Whiting, A. Leo and R.S. Taft, *J. Chem. Soc., Perkin Trans. II*, 1777 (1994).
13. Y. Wang, D. Han, M. Tian and K.H. Row, *Korean J. Chem. Eng.*, **26**, 812 (2009).
14. M.P. Marszall, T. Baczek and R. Kaliszan, *Anal. Chim. Acta*, **547**, 172 (2005).
15. M. Tian and K.H. Row, *Chem. Res. Chinese Univ.*, **25**, 306 (2009).
16. Y. Jin and K.H. Row, *J. Liq. Chromatogr. Rel. Technol.*, **30**, 335 (2007).
17. C.H. Jin, J.W. Lee and K.H. Row, *Korean Chem. Eng. Res.*, **44**, 555 (2006).
18. G. Jin, Z. Guo, F. Zhang, X. Xue, Y. Jin and X. Liang, *Talanta*, **76**, 522 (2008).
19. M. Molíková, M.J. Markuszewski, R. Kaliszan and P. Jandera, *J. Chromatogr. A*, **1217**, 1305 (2010).