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Effect of hydrophobic side-chains on the solvation of imidazolium salts

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ABSTRACT: The chemical shifts of the aromatic hydrogens of 12 symmetrical imidazolium salts were determined in different deuterated solvents. Based on the magnitude of the chemical shift change for the hydrogens of the imidazolium ion in the various solvents, relationships were developed to determine the relative solute/solvent interactions for these compounds. Owing to different degrees of interactions involving the aromatic hydrogens of the imidazolium cations and anions, there is a variation in the interaction of the hydrogens with the solvent molecules. The intimate interaction that exists between the hydrogens of the imidazolium cation and the BF_4^- anion results in the BF_4^- salts being less solvated compared with salts containing BF_6^- and SbF_6^- anions. For imidazolium salts that contain C_2H_5, C_4H_9 and C_8H_{17} side-chains bonded in the 1 and 3 positions, the interaction between H2 and the solvents was observed to be greater than for imidazolium salts with $C_{16}H_{33}$ substituents. On the other hand, for imidazolium salts that have $C_{16}H_{33}$ substituents the interaction between H2 and the solvents is similar to that for H4 and H5. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: ionic liquids; solvation effects; ^{1}H NMR spectroscopy

INTRODUCTION

Ambient-temperature ionic liquids have been utilized in a wide range of chemical applications since they were first discovered in 1951.[1] Ionic liquids offer a very attractive alternative to conventional solvents for organic reactions.[2] They are thermally stable over a very wide temperature range and some maintain their liquid state at temperatures as high as 200 °C.[3] Ionic liquids have no detectable vapor pressures and, as a result, have been substituted for molecular solvents that often have harmful vapors for a wide variety of reactions. In addition, ionic liquids have been shown to have tremendous influence on the outcome of reactions in a number of ways, such as higher reaction rates and better reaction control.[4] Some polar molecular solvents such as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF), which are presently being used to provide polar environments for most organic reactions, present tremendous difficulty for separation of the product from the reaction mixture, and the cost to dispose of these solvents is typically very high.[5] The unique features of ionic liquids contribute to them fast becoming the solvent of choice for many organic reactions.

Because the field of ionic liquids is still in its infancy, a systematic analysis of the properties of these new designer solvents and the effects that they have on reactions has not been accomplished. One type of ionic liquid that has gained widespread usage consists of 1-alkyl-3-methylimidazolium salts. It is known that variation of the nature of alkyl groups bonded to the organic cation can be used to fine-tune the properties of ionic liquids so that they meet specific solvent properties to influence the outcome of various organic reactions.[6] We have shown recently that the ionic liquid 1-*n*-butyl-3-methylimidazolium tetrafluoroborate can be used as an effective solvent for the synthesis of compounds that contain highly functionalized groups.[7] An important property of solvents is their ability to have different types of interactions with reactants, intermediates and products of various reactions.[8,9] It has been shown that 1-*n*-ethyl-3-methylimidazolium (EMI^+) salts are capable of forming hydrogen bonds to basic solutes,[10] but the effects that different anions and side-chains have on the relative strengths of such interactions are not known. In this study, the sensitivity of the interactions involving the hydrogens of different imidazolium salts and their solvent environments is investigated.

EXPERIMENTAL

The synthesis of imidazolium hexafluoroantimonate, hexafluorophosphate and tetrafluoroborate salts was

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Table 1. The H^1 chemical shift values of 1,3-dialkylimidazolium salts in different deuterated solvents at 298 K (solution concentrations are 0.45 ± 0.01 mol l^{-1} for all compounds)

		$R = C_2H_5$		$R = C_4H_9$		$R = C_8H_{17}$		$R = C_{16}H_{33}$	
Solvent-*d*[a]	X^-	δH2	δH4, 5	δH2	δH4, 5	δH2	δH4, 5	δH2	δH4, 5
AN	SbF_6^-	8.429	7.375	8.418	7.372	8.416	7.374	8.427	7.382
	PF_6^-	8.437	7.387	8.434	7.382	8.438	7.377	8.451	7.391
	PF_4^-	8.533	7.404	8.534	7.410	8.500	7.395	[b]	[b]
TFA	SbF_6^-	8.637	7.564	[b]	[b]	8.756	7.583	[b]	[b]
	PF_6^-	8.677	7.584	8.588	7.480	8.494	7.390	[b]	[b]
	PF_4^-	[b]	[b]	8.754	7.650	8.612	7.491	[b]	[b]
HOAc	SbF_6^-	8.583	7.485	8.611	7.502	8.620	7.507	[b]	[b]
	PF_6^-	8.650	7.505	8.639	7.509	8.702	7.527	[b]	[b]
	PF_4^-	[b]	[b]	8.767	7.553	8.790	7.559	[b]	[b]
MeOH	SbF_6^-	8.804	7.565	8.817	7.566	8.800	7.557	[b]	[b]
	PF_6^-	8.782	7.563	8.776	7.557	8.817	7.571	[b]	[b]
	PF_4^-	8.856	7.611	8.880	7.615	8.907	7.618	[b]	[b]
Acetone	SbF_6^-	9.001	7.745	9.015	7.746	8.987	7.727	8.960	7.711
	PF_6^-	8.924	7.709	8.953	7.726	9.012	7.751	9.040	7.816
	PF_4^-	8.999	7.749	9.009	7.751	9.047	7.765	[b]	[b]
DMSO	SbF_6^-	9.157	7.765	9.169	7.768	9.175	7.758	9.204	7.763
	PF_6^-	9.136	7.758	9.152	7.756	9.170	7.770	9.184	7.761
	PF_4^-	9.123	7.765	9.131	7.762	9.175	7.794	9.198	7.788
DMF	SbF_6^-	9.300	7.908	9.316	7.916	9.319	7.903	9.318	7.893
	PF_6^-	9.240	7.873	9.268	7.888	9.334	7.931	9.289	7.892
	PF_4^-	9.257	7.907	9.248	7.904	9.312	7.937	9.356	7.932
Benzene	SbF_6^-	[b]	[b]	[b]	[b]	[b]	[b]	7.935	6.678
	PF_6^-	[b]	[b]	[b]	[b]	[b]	[b]	8.261	6.855
	PF_4^-	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
$CDCl_3$	SbF_6^-	[b]	[b]	[b]	[b]	8.460	7.315	8.444	7.330
	PF_6^-	8.347	7.299	[b]	[b]	8.588	7.324	8.517	7.321
	PF_4^-	[b]	[b]	[b]	[b]	8.803	7.372	8.892	7.388

[a] AN, acetonitrile; TFA, trifluoroacetic acid; HOAc, acetic acid; MeOH, methanol; DMSO, dimethyl sulfoxide; DMF, dimethyl formamide.
[b] Insoluble or partially soluble in the deuterated solvent.

carried out as described in the literature.[11] All products were recrystallized from ethanol or acetone. For each salt, water and other volatile solvents were removed by six cycles of freeze, pump and thaw (8 mmHg and 77 K); compounds 3, 6, 9 and 12 were dried at 50 °C followed by freeze–thaw purification. (Present methods of purification of these compounds appear not to give the purity predicted by the elemental analysis for the tetrafluoroborate salts, but future efforts will be directed at finding new and improved methods to purify these compounds. However, any impurities determined by elemental analysis for these salts do not appear to affect significantly the NMR results of these compounds.) All NMR solutions were prepared in a dry-atmosphere glovebox, and the residual solvent for each sample was used as internal standard for the NMR data shown in Table 1. The concentration of all salts was 0.45 ± 0.01 mol l^{-1}. The NMR and infrared spectra of previously synthesized compounds matched those reported in the literature.[11] The ^{1}H NMR spectra were recorded on a Varian Gemini 500 MHz FT-NMR spectrometer. Elemental analysis was carried out by Quantitative Technologies Inc., New Jersey. The Minitab multilinear regression analysis computer program (State College, PA) was used to obtain the correlation equations shown in Table 2.

1,3-Diethylimidazolium hexafluoroantimonate (compound 1). The percentage yield of a yellow liquid product was 87%. ^{1}H NMR (acetone-d_6): δ 9.06 (s,1H), 7.65 (d, 2H $J = 1.59$ Hz), 4.37 (q, 4H, $J = 6.96$ Hz), 1.56 (t, 6H, $J = 7.33$). IR (NaCl): 3245, 3060, 3000, 1585, 1245, 1230, 745, 700 cm^{-1}. Anal calc. for $C_7H_{13}N_2SbF_6$ (360.943): C 23.29, H 3.63, N 7.76; found C 23.43, H 3.54, N 7.59.

1,3-Diethylimidazolium hexafluorophosphate (compound 2). The percentage yield of a white powder product was 76% and m.p. = 58–61 °C (lit 63–66 °C).[11a] ^{1}H NMR (acetone-d_6): δ 9.06 (s,1H), 7.78 (d, 2H $J = 1.7$ Hz), 4.40 (q, 4H, $J = 6.84$), 1.56 (t, 6H, $J = 7.33$ Hz). IR(NaCl): 3255, 3056, 3000, 2350, 1590, 1250, 1235, 810, 750, 5560 cm^{-1}.

1,3-Diethylimidazolium tetrafluoroborate (compound 3). The percentage yield of a white powder product was 82% and m.p. = 38–40 °C. ^{1}H NMR (acetone-d_6): δ 9.10 (s,1H), 7.67 (d, 2H $J = 1.59$ Hz), 4.39 (q, 4H, $J = 7.33$ Hz), 1.54 (t, 6H, $J = 7.33$). IR (NaCl): 3240, 3050, 3000, 1590, 1250, 1180, 1070, 745 cm^{-1}. Anal calc. for $C_7H_{13}N_2BF_4$ (211.998): C 39.65, H 6.18, N 13.21; found C 39.21, H 6.31, N 10.08.

Table 2. Statistics for the correlation equations ($y = mx + c$), which show the relationships between the chemical shifts for the aromatic hydrogens of different substituted imidazolium salts, the structures of the imidazolium salts are shown in Fig. 1

Entry	R	X^-	y	x	m (slope)	c	R	n	SD
1	C_2H_5	SbF_6^-	δH_2	δH_5	1.71	−4.23	0.961	7	0.0693
2	C_2H_5	PF_6^-	δH_2	δH_5	1.62	−3.49	0.968	8	0.0604
3	C_2H_5	BF_4^-	δH_2	δH_5	1.45	−2.20	0.982	5	0.0434
4	C_4H_9	SbF_6^-	δH_2	δH_5	1.69	−3.99	0.988	6	0.0577
5	C_4H_9	PF_6^-	δH_2	δH_5	1.69	− 4.01	0.971	7	0.0529
6	C_4H_9	BF_4^-	δH_2	δH_5	1.47	− 2.35	0.924	7	0.0740
7	C_8H_{17}	SbF_6^-	δH_2	δH_5	1.61	−4.40	0.974	7	0.0560
8	C_8H_{17}	PF_6^-	δH_2	δH_5	1.61	− 3.45	0.993	8	0.0487
9	C_8H_{17}	BF_4^-	δH_2	δH_5	1.46	− 2.28	0.989	8	0.0496
10	$C_{16}H_{33}$	SbF_6^-	δH_2	δH_5	1.17	0.02	0.929	6	0.1587
11	$C_{16}H_{33}$	PF_6^-	δH_2	δH_5	1.03	1.06	0.941	6	0.1642
12	$C_{16}H_{33}$	BF_4^-	δH_2	δH_5	0.83	2.72	0.996	3	0.0277

1,3-Dibutylimidazolium hexafluoroantimonate (compound 4). The percentage yield of a pale-yellow liquid product was 98.6%. ^1H NMR ($CDCl_3$): δ 10.50 (s,1H), 7.97 (d, 2H, $J = 1.59$ Hz), 4.47 (t, 4H, $J = 7.33$ Hz), 1.95 (q, 4H, $J = 7.45$ Hz), 1.38(q, 4H, $J = 7.57$ Hz), 0.95(t, 6H, $J = 7.3$ Hz). IR (NaCl): 3150, 3010, 2940, 1260, 735 cm^{-1}. Anal calc. for $C_{11}H_{21}N_2SbF_6$ (417.051): C 31.67, H 5.07, N 6.71; found C 31.62, H 5.00, N 6.64.

1,3-Dibutylimidazolium hexafluorophosphate (compound 5). The percentage yield of a pale-yellow liquid product was 96%. ^1H NMR ($CDCl_3$): δ 8.58 (s,1H), 7.31 (d, 2H, $J = 1.71$ Hz), 4.17 (t, 4H, $J = 7.33$ Hz), 1.85 (q, 4H, $J = 7.57$ Hz), 1.35(q, 4H, $J = 7.69$ Hz), 0.94(t, 6H, $J = 7.33$ Hz). IR (NaCl): 3180, 3050, 2960, 1550, 1260, 850, 725 cm^{-1}.

1,3-Dibutylimidazolium tetrafluoroborate (compound 6). The percentage yield of a pale-yellow liquid product was 70%. ^1H NMR ($CDCl_3$): δ 9.05 (s,1H), 7.33 (s, 2H), 4.21 (t, 4H, $J = 7.39$ Hz), 1.86 (q, 4H, $J = 7.56$ Hz), 1.35(q, 4H, $J = 7.56$ Hz), 0.94(t, 6H, $J = 6.36$ Hz). IR (NaCl): 3010, 2950, 1260, 1090, 725 cm^{-1}. Anal calc. for $C_{11}H_{21}N_2BF_4$ (268.106): C 49.27, H 7.89, N 10.44; found C 48.32, H 7.89, N 10.18.

1,3-Dioctylimidazolium hexafluoroantimonate (compound 7). The percentage yield a pale-yellow liquid product was 96.4%. ^1H NMR ($CDCl_3$): δ 9.01 (s,1H), 7.32 (d, 2H $J = 1.59$ Hz), 4.22 (t, 4H, $J = 7.45$ Hz), 1.89 (q, 4H, $J = 7.20$ Hz), 1.30(m, 24H), 0.87(t, 6H, $J = 6.96$ Hz). IR (NaCl): 3140, 3000, 2975, 2350, 1270, 740 cm^{-1}. Anal calc. for $C_{19}H_{37}N_2SbF_6$ (529.267): C 43.11, H 7.04, N 5.29; found C 45.03, H 7.46, N 5.56.

1,3-Dioctylimidazolium hexafluorophosphate (compound 8). The percentage yield of a pale-yellow liquid product was 98.8%. ^1H NMR ($CDCl_3$): δ 9.25 (s,1H), 7.32 (d, 2H $J = 1.34$ Hz), 4.22 (t, 4H, $J = 7.45$ Hz), 1.89 (q, 4H, $J = 7.20$ Hz), 1.30 (m, 24H), 0.87 (t, 6H, $J = 6.96$ Hz). IR (NaCl): 3050, 2990, 2900, 2260, 1410, 1260, 720 cm^{-1}.

1,3-Dioctylimidazolium tetrafluoroborate (compound 9). The percentage yield of a pale-yellow liquid product was 96%. ^1H NMR ($CDCl_3$): δ 10.37 (s,1H), 7.31 (d, 2H $J = 1.59$ Hz), 4.35 (t, 4H, $J = 7.44$ Hz), 1.94 (q, 4H, $J = 7.20$ Hz), 1.30 (m, 24H), 0.87 (t, 6H, $J = 6.83$ Hz). IR (NaCl): 3140, 3000, 2970, 2940, 1270, 735 cm^{-1}. Anal calc. for $C_{19}H_{37}N_2BF_4$ (380.32): C 60.00, H 9.80, N 7.36; found C 53.82, H 9.16, N 6.66.

1,3-Dihexadecylimidazolium hexafluoroantimonate (compound 10). The percentage yield of a white solid product was 98.6% m.p. = 62–64 °C. ^1H NMR ($CDCl_3$): δ 8.57 (s,1H), 7.26 (s, 2H), 4.17 (t, 4H, $J = 7.47$ Hz), 1.87 (q, 4H, $J = 7.32$ Hz), 1.25 (m, 52H), 0.87 (t, 6H, $J = 6.84$ Hz). IR (NaCl): 3055, 2935, 2890, 1260, 728 cm^{-1}. Anal calc. for $C_{35}H_{69}N_2SbF_6$ (753.699): C 55.77, H 9.22, N 3.71; found C 56.18, H 9.21, N 3.71.

1,3-Dihexadecylimidazolium hexafluorophosphate (compound 11). The percentage yield of a white solid product was 96% and m.p. = 70–73 °C. ^1H NMR ($CDCl_3$): δ 8.67 (s,1H), 7.26 (d, 2H, 1.59), 4.14 (t, 4H, $J = 7.47$ Hz), 1.86 (q, 4H, $J = 7.08$), 1.25 (m, 52H), 0.87 (t, 6H, $J = 6.84$). IR (NaCl): 3100, 2920, 2875, 1270, 850, 730 cm^{-1}. Anal calc. for $C_{35}H_{69}N_2PF_6$ (662.91): C 63.41, H 10.49, N 4.22; found C 63.65, H 10.48, N 4.06.

1,3-Dihexadecylimidazolium tetrafluoroborate (compound 12). The percentage yield of a light-yellow solid product was 70% and m.p. = 67–70 °C. ^1H NMR ($CDCl_3$): δ 9.69 (s,1H), 7.31 (d, 2H, $J = 1.34$ Hz), 4.27 (t, 4H, $J = 7.33$ Hz), 1.90 (q, 4H, $J = 7.32$), 1.25 (m, 52H), 0.87 (t, 6H, $J = 6.84$ Hz). IR (NaCl): 3060, 2933, 2875, 2300, 1250, 730 cm^{-1}. Anal calc. for $C_{35}H_{69}N_2BF_4$ (604.754): C 69.51, H 11.50, N 4.63; found C 68.55, H 11.18, N 4.38.

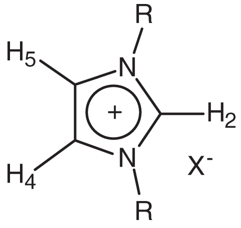

Figure 1. Ionic salts; R and X^- are shown in Table 1

RESULTS AND DISCUSSION

The ^{1}H NMR chemical shifts of the aromatic protons of 12 ionic salts, where the symmetrical imidazolium cations contain alkyl side-chains of different lengths (Fig. 1), were determined in different deuterated solvents and the results are shown in Table 1. Owing to the limited or lack of solubility of the ionic salts investigated in deuterated water, they were not included in this study.[12]

It is known that the chemical shifts of the imidazolium ring protons are dependent on the nature of the anion and the concentration of the salt, and that the H2 proton is the most sensitive compared with the H4 and H5 protons.[13] As a result, the extent of interactions involving acidic hydrogens and basic solvents[14] influences the chemical shifts of the hydrogen. The chemical shifts of acidic hydrogens that are involved in such interactions are further downfield than hydrogens that are not.[15] Because the change in chemical shifts can be used to assess the nature of such interactions, the chemical shifts of the protons of the various imidazolium salts were determined in different deuterated solvents at the same concentration and temperature. From the results shown in Table 1 it is obvious that the chemical shifts of the aromatic hydrogens are solvent dependent and that they vary as a function of the nature of the anion and the length of the alkyl side-chain bonded to the imidizolium cation.

Recently, we have utilized the relationship $y = mx + c$ (where y and x are the chemical shifts of any two hydrogens of the imidazolium cation, m is the slope and c is the intercept) to estimate the sensitivity of the interaction between the aromatic hydrogens and the solvent medium.[16] Relationships that give slopes of unity imply that the environments of the hydrogens being considered (as measured by the chemical shifts) are similar, whereas non-unity slopes imply that the environments of the hydrogens being considered are different. A large slope implies that one of the hydrogens being considered is more sensitive to changes in the solvent environment than the other hydrogen. Because the chemical shifts of H4 and H5 are the same, the relationships for H2/H4 are the same as for H2/H5; the statistics for the relationships between the imidazolium protons of this study are shown in Table 2. For these relationships, a standard deviation of < 0.1642 and $0.996 > R > 0.924$ were obtained. It is obvious from the slopes shown in Table 1 that they vary both as a function of the nature of the side-chains and also of the anions of the salts examined.

Solvation effects

From Table 2, the slopes are larger for the SbF_6^- and PF_6^- salts compared with those of BF_4^- salts. The interaction between the larger, more polarizable PF_6^- and SbF_6^- anions and H2 (relative to H4 and H5) is not as great as that involving the less polarizable BF_4^- anion. Because H2 is bonded to a carbon that is situated between two electronegative nitrogen atoms, it will be the most sensitive to interactions involving the anions in different solvent environments. As a result, the SbF_6^- and PF_6^- salts are better hydrogen-bond acceptors than the BF_4^- salts. This observation is consistent with that reported for 1-butyl-3-methylimidazolium salts.[16,17] Another factor that affects the solvation of compounds is solvent polarity, and various descriptors have been developed from thermodynamic and spectroscopic data to evaluate this effect.[18] Preliminary analysis of the NMR data shown in Table 1 using the solvatochromic parameters[19] in multilinear relationships shows that the solvent dipolarity/polarizability property plays a greater role in solvation of SbF_6^- salts compared with BF_4^- salts. (From multilinear relationships involving the solvents' dipolarity/polarizability (π^*), hydrogen-bond acidity (α) and hydrogen-bond basicity (β) with chemical shift variations, a larger slope was observed for π^* for SbF_6^- salts compared with BF_4^- salts.) A detailed linear solvation energy relationship (LSER) analysis is presently being carried out in our laboratory to understand better the nature of the solvation of these salts.

Preliminary concentration- and temperature-dependence studies of these compounds carried out in our laboratory show that the dependence of the chemical shift of H2 on the concentration of the salt is not significant; but as the temperature varies the chemical shift of H2 varies also. For example, the chemical shift of H2 of compound 1 in DMF moves upfield by 0.17 ppm over the temperature range 0–120 °C. These results suggest that intermolecular hydrogen bonding involving these compounds is not significant, but the interaction involving the cation and the anion is temperature dependent.

Because the slopes for compounds 10, 11 and 12 are similar and close to unity, the implication is that the average environment of H2 and H4/H5 for these salts is similar. Aggregation and π-stacking of these molecules with longer side-chains could give rise to the similarity of the environment experienced by all the hydrogens of the hexadecyl salts. Similar stacking has been used to explain the intramolecular interactions that exist for molten salts.[20] The slopes for all the compounds are greater than unity, except compound 12, which has a slope of slightly less than unity. From Table 2, compound 12 is not soluble in a wide selection of solvents, hence the value of

0.83 for the slope (which was derived from three data points) may not be as reliable as those determined for the other compounds.

CONCLUSION

There is competition for the interaction of aromatic hydrogens of imidazolium salts for the solvent molecules and the anions. There is an observable difference between the interaction involving the more polarizible PF_6^- and SbF_6^- anions with H2 compared with the interaction with the harder BF_4^- anion. A strong interaction between the anion and the hydrogens results in reduced interaction of the hydrogens with the solvent molecules. For imidazolium salts that have long hydrophobic side-chains in positions 1 and 3, the interaction between the solvent or the counter-anion and the aromatic hydrogens is much less than that experienced by imidazolium salts where the side-chains are short and less hydrophobic. For imidazolium salts that have $C_{16}H_{33}$ substituents, the interaction between H2 and the solvents is similar to that of H4 and H5, which may be caused by aggregation among these compounds.

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