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Mixed Valence Compounds as Probes to Determine the Polarity of 1-Butyl-3-methylimadazolium Ionic Liquids

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Radical cations and dications of three bishydrazines belonging to the Class II mixed valence compounds have been generated, either spontaneously or by oxidation with $AgSbF_6$, in two 1-butyl-3-methylimidazolium (4^+) ionic liquids having BF_4^- and PF_6^- as counterions. The optical spectra of these intermediates have allowed evaluation of Marcus' reorganization energy λ_s, a parameter that is directly proportional to the solvent polarity. Remarkable differences in λ_s, as large as 600 cm^{-1}, have been observed as a function of the counterion, with these data providing support for the observed differences between both ionic liquids ($4^+BF_4^-$ and $4^+PF_6^-$) in catalysis. However, in terms of polarity, the λ_s values rank the hydrophilic $4^+BF_4^-$ as being similar to dimethyl sulfoxide and dimethylformamide, while the polarity of hydrophobic $4^+PF_6^-$ is analogous to acetonitrile. Overall, our results indicate that ionic liquids are not exceptional liquids in terms of polarity.

Introduction

Room-temperature ionic liquids are presently attracting considerable attention as promising solvents for green chemistry because of the possibility to conduct catalytic reactions in a homogeneous phase while still being able to recover and reuse the catalysts. [1–6] The zero vapor pressure of ionic liquids and their ability to dissolve a large variety of organic compounds make them good candidates to replace conventional volatile organic solvents.

In this context, it has been frequently claimed that the presence of naked ions in these liquids should make them behave as very polar media, with this polarity being commonly invoked to justify remarkable effects in catalysis. [7–8] The ease of generation, stability, and long lifetimes of ionic intermediates have also been established using photochemical means. [8–10] Considering the interest in obtaining relevant physicochemical data to gain understanding on the specific features arising from the polarity of ionic liquids, we describe herein the work using mixed valence compounds to estimate the effective polarity of the two most commonly used ionic solvents.

Mixed valence compounds have at least two charge-bearing units, **M**, that are connected by a bridge, **B**, and are at an oxidation level where the charges on the **M** groups might be different. When the charges on the **M** groups are different, M_2B^+ radical cations may be usefully considered to be ^+M–B–$M \varsigma M$–B–M^+ electron-transfer systems, and are called Robin–Day Class II compounds. [11] Hush pointed out that the lowest energy optical transition maximum, $\bar{\nu}_{max}$, for Class II mixed valence compounds corresponds to the Marcus reorganization energy, λ, [12–13] and also showed how to evaluate H_{ab}, the second parameter needed to calculate the rate constant for adiabatic electron transfer between the **M** groups using the

classical two-state model employed by Marcus. [14] By making use of appropriate organic **M** groups as well as bridges, it has been possible to make examples for which the rate constant can be measured by electron spin resonance, which has shown that Hush's optical evaluation of λ and H_{ab} produces surprisingly accurate predictions of electron-transfer rate constant for several examples, including bishydrazine 1^+. [15,16]

In this work, we determined $\bar{\nu}_{max}$ for bishydrazines **1–3** in two commonly used ionic liquids, the hexafluorophosphate and tetrafluoroborate salts of the 1-butyl-3-methylimidazolium cation 4^+ (Figure 1).

Compounds **1–3** are well-known examples of Class II mixed valence radical cations to which Marcus's equation, $\bar{\nu}_{max} = \lambda = \lambda_s + \lambda_v$, can be applied. The internal vibrational contribution λ_v, is assumed to be constant and independent of the medium, but the solvent contribution, λ_s, is usually described as increasing with solvent polarity. This work provides a measure of how λ_s for these compounds compares with those for ordinary solvents, giving an estimation of ionic liquid polarities using the size of λ_s as the criterion.

Results

$4^+BF_4^-$ and $4^+PF_6^-$ are considered paradigmatic examples of hydrophilic and hydrophobic ionic liquids, respectively. [17] Apparently, the difference in the fluorine content of both liquids is responsible for this contrasting behavior that is reflected, for instance, in their water miscibility and their tendency to adsorb moisture from the atmosphere. Also, the contrasting behavior between $4^+BF_4^-$ and $4^+PF_6^-$ in catalytic reactions has been attributed to differences in their polarity. [18] Therefore, it is of interest to obtain $\bar{\nu}_{max}$ values for mixed valence compounds in these ionic liquids.

Spontaneous oxidation of hydrazines **1** and **2** to mixtures of mono- and dications is observed upon dissolving them in ionic liquids in the absence of any external oxidizing reagent. In the case of bishydrazine **2**, exclusive formation of the radical cation

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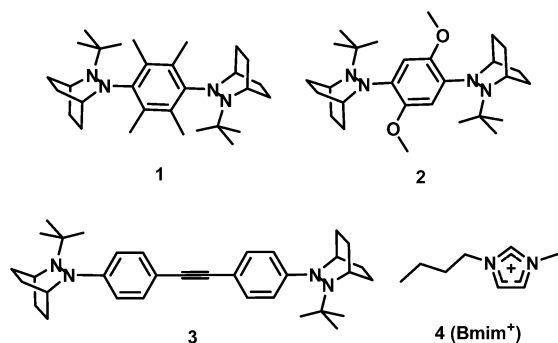† Universidad Politécnica de Valencia.

‡ University of Wisconsin.

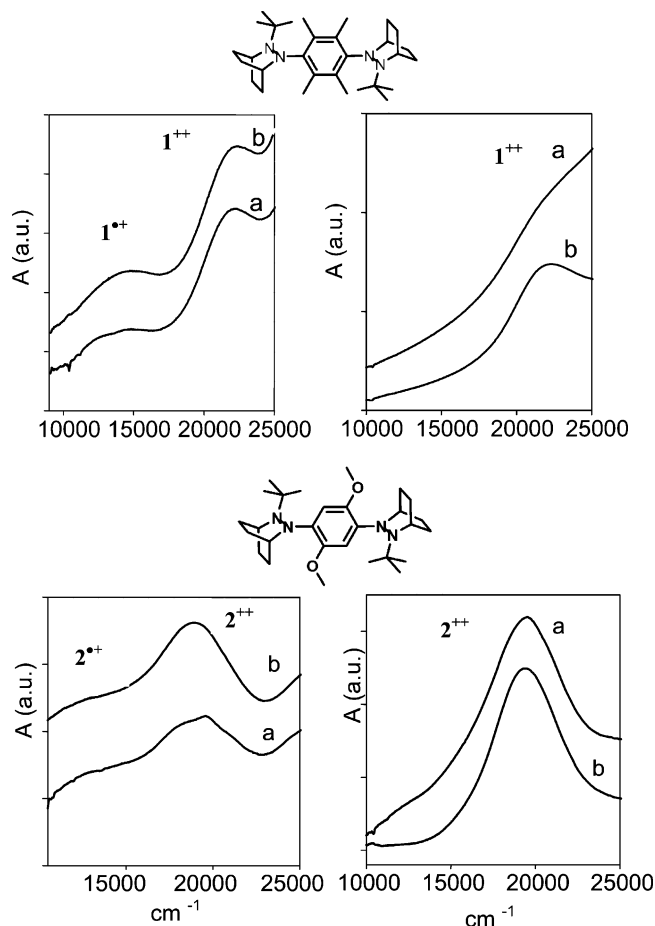**Figure 1.** Structures of bishydrazines **1**−**3** and of the 1-butyl-3-methylimidazolium cation **4**⁺.

Figure 2. Left: UV−visible absorption spectra of the cation (+)/dication (++) of hydrazines **1** (top) and **2** (bottom) in ionic liquids (a) **4**⁺PF₆⁻ and (b) **4**⁺BF₄⁻ recorded with no added oxidant. Right: UV−visible absorption spectra of the dication (++) of hydrazines **1** (top) and **2** (bottom) in ionic liquids (a) **4**⁺PF₆⁻ and (b) **4**⁺BF₄⁻ obtained after the addition of an excess of AgSbF₆.

2•⁺ in ionic liquids could be accomplished in the dark upon the addition of AgSbF₆ as oxidant. It was observed that exposure to ambient light of a solution of bishydrazine **2** in **4**⁺BF₄⁻ promotes oxidation with formation of the mono- and dication. The effect of light causing photoionization in polar solvents is well-documented in photochemistry.[19−21] However, in this case, it is remarkable that ambient light is sufficient to produce this effect to a significant extent.

The spectra of the radical cations and dications derived from **1** and **2** partially overlap, making it difficult to estimate accurate $\bar{\nu}_{max}$ values for **1**•⁺ and **2**•⁺ without performing band deconvolution of the spectra. In contrast, optical spectra of the dications **1**²⁺ and **2**²⁺, free from their corresponding radical cations, can be recorded easily after complete oxidation of **1** and **2** using an excess of Ag⁺. Figure 2 shows the transmission visible spectra recorded for compounds **1** and **2** after dissolving them in ionic liquids **4**⁺BF₄⁻ and **4**⁺PF₆⁻ and after the addition of 1 equiv of AgSbF₆.

In the case of compound **3**, no spontaneous oxidation was observed upon dissolving it in ionic liquids **4**⁺BF₄⁻ and **4**⁺PF₆⁻. This result is in agreement with the higher potential needed to effect the oxidation of compound **3** as shown in Table 1. Worth noting is the low oxidation potential of bishydrazine **1** that makes its spontaneous oxidation very easy.

Compound **3** could, however, be oxidized using equimolar or excess amounts of AgSbF₆. As can be observed in Figure 3 for hydrazine **3**, the bands are rather broad in ionic solvents and are reported at an accuracy of ±100 cm⁻¹.

Table 2 lists the measured band maxima for the mixed valence radical cations and dications derived from compounds **1**−**3**. For the sake of comparison, Table 2 also contains reported $\bar{\nu}_{max}$ values for these species measured in acetonitrile. It is remarkable that the transition energies are 600 cm⁻¹ higher in the tetrafluoroborate salt than in the hexafluorophosphate salt for **1**⁺ and **3**⁺, but only 200 cm⁻¹ higher for **2**⁺.

Discussion

Solid **1**•⁺Ph₄B⁻ is one of the very few mixed valence compounds that does not disproportionate to neutral species and dications upon crystallization. Synthesis of solid **1**•⁺Ph₄B⁻ has allowed for obtaining its X-ray structure,[22] as well as its optical spectrum in the solid state in transparent solid matrices, using diffuse reflectance spectroscopy.[23] The solution spectrum of **1**⁺ has also been determined in several solvents.[24] The λ_v for **1**⁺ has been estimated at 10 100 cm⁻¹ from the effect of solvent on $\bar{\nu}_{max}$[24] and at 9250 cm⁻¹ from its resonance Raman spectrum.[25] Therefore, the values in Table 2 indicate that λ_s in acetonitrile and **4**⁺PF₆⁻ is about 4000 (or 4850) cm⁻¹, and increases 600 cm⁻¹ in **4**⁺BF₄⁻. Figure 4 shows a graphical

TABLE 1: Redox Potentials and Differences of 1−3 in CH₂Cl₂ (0.1M TBAP) vs SCE[a]

compound	E°_1 (mV)	E°_2 (mV)	$\Delta E^{\circ}_{(2-1)}$
1[b]	−115	234	349
2[c]	138	532	394
3[d]	320	410	90

[a] Using ferrocene or decamethylferrocene as the internal standard. [b] Scan rate = 20 mV/s. [c] Scan rate = 25 mV/s. [d] Scan rate = 100 mV/s. Overlapping first and second redox waves were deconvoluted using computer simulation

comparison of $\bar{\nu}_{max}$ values for **1**⁺ in various solvents[24,26] as well as for solid **1**•⁺Ph₄B⁻ in various matrices.

Although it has been widely assumed that λ_s for Class II mixed valence compounds would be directly proportional to the dielectric continuum "solvent polarity" parameter $\gamma = 1/n^2 - 1/\epsilon_S$, where n is the refractive index and ϵ_S is the static dielectric constant of the solvent,[13] this is not the case, because γ is largest for acetonitrile, but $\bar{\nu}_{max}$ is larger in acetone, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Good correlations for several bishydrazine radical cations are found when the noncontinuum quantity Gutmann solvent donicity is included in addition to γ and a constant (interpreted as λ_v).[24] The counterion for **4**⁺ changes λ_s noticeably, with the larger and more fluorous PF₆⁻ anion causing a remarkable 600 cm⁻¹ shift toward smaller $\bar{\nu}_{max}$ values compared to the smaller and less fluorous BF₄⁻ anion. The size of the effect is about as

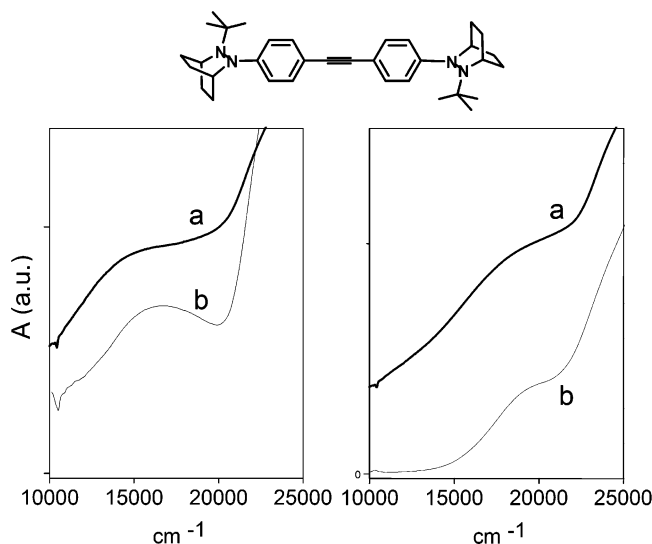Mixed Valence Compounds Determine Solvent Polarity

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Figure 3. Left: UV−visible absorption spectra of the cation (+) of hydrazine **3** in ionic liquids (a) **4**$^+$PF$_6$$^-$ and (b) **4**$^+$BF$_4$$^-$ obtained after the addition of 1 equiv of AgSbF$_6$. Right: UV−visible absorption spectra of the dication (++) of hydrazine **3** in ionic liquids (a) **4**$^+$PF$_6$$^-$ and (b) **4**$^+$BF$_4$$^-$ obtained after the addition of an excess of AgSbF$_6$.
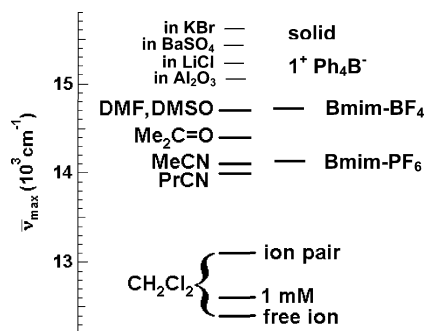

Figure 4. Comparison of $\bar{\nu}_{max}$ values for **1**$^+$ in ordinary solvents, ionic liquids, and for solid **1**$^{•+}$Ph$_4$B$^-$ in various matrices.

TABLE 2: Comparison of $\bar{\nu}_{max}$ (cm^{-1}) Values in Acetonitrile and Ionic Solvents

compound	solvent	monocation	dication
1	CH$_3$CN	14 100	22 100
	4$^+$PF$_6$$^-$	14 100	22 100
	4$^+$BF$_4$$^-$	14 700	22 200
2	CH$_3$CN	12 800	19 500
	4$^+$PF$_6$$^-$	12 800	19 500^a 19 800^b
	4$^+$BF$_4$$^-$	13 000	19 300^b 19 400^a
3	CH$_3$CN	16 000	19 000
	4$^+$PF$_6$$^-$	15 900^b	18 900^c
	4$^+$BF$_4$$^-$	16 500^b	19 400^c

^{a} Without Ag$^+$. ^{b} 1 equiv of Ag$^+$ used. ^{c} Excess of Ag$^+$ used.

large as that for the solvent donicity increase of DMSO or DMF compared to acetonitrile (for which increased donicity more than offsets the smaller γ values in these solvents). The experimental data point to an essentially complete ion pairing for bishydrazine radical cations in the ionic liquids. This seems reasonable in view of the high anion concentration present in the medium. Furthermore, it is worth noting that λ_s remains notably smaller in the ionic liquids than in crystalline **1**$^{•+}$Ph$_4$B$^-$, despite the latter having a larger anion (25 heavy atoms instead of 5 or 7). This is presumably a result of the absence of the accompanying imidazolium cation that is present in the ionic liquids.

Thus, the measurements using the mixed valence compounds reveal the remarkable influence of the fluorinated anion on the λ_s, with this fact being in good agreement with prior observations

in catalysis. However, in terms of polarity, the λ_s values rank the hydrophilic **4**$^+$BF$_4$$^-$ as being similar to DMSO and DMF, while the polarity of hydrophobic **4**$^+$PF$_6$$^-$ is analogous to that of acetonitrile. Overall, our results indicate that ionic liquids are not exceptional liquids in terms of polarity.

Experimental Section

The ionic liquids Bmim-PF$_6$ and Bmim-BF$_4$ (Solvent Innovation) and AgSbF$_6$ (Aldrich) were commercial samples. The bishydrazine **1** was synthesized according to the experimental procedure described in the literature.[22]

1,4-Bis(2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)-2,5-dimethoxybenzene (2). 1,4-Diiodo-2,5-dimethoxybenzene (185 mg, 0.47 mmol, obtained by Suzuki iodination of 1,4-dimethoxybenzene) was dissolved in tetrahydrofuran (THF) (3 mL) in an oven-dried 50 mL Schlenk flask. The mixture was cooled to −78 °C and *t*-BuLi (1.74 M in pentane, 1.08 mL, 1.88 mmol) was added dropwise. A white suspension formed with some yellow solid on the bottom of the flask. After stirring for 2 h, the yellow 2-*t*-Bu-2,3-diazabicyclo[2.2.2]oct-2-ene iodide (290 mg, 0.99 mmol) was added. The cooling bath was gradually lowered and removed. The mixture was stirred for 2 h at room temperature, quenched with water (15 mL), and extracted with toluene (2 × 25 mL) to give 0.22 mg of off-white solid. The solid was refluxed with 5 mL of EtOH and filtered, washed well with EtOH (ca. 15 mL), and air-dried to give the product as a white solid (140 mg, 60%), mp = 212 °C. MS: 470.3612 *m/e*, *I* = 20%, calcd for C$_{28}$H$_{46}$N$_4$O$_2$ 470.3621. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.812 and 7.805 (s, 2H, Ar*H*), 4.05 and 4.01 (m, 2H, NC*H*), 3.72 and 3.70 (s, 6H, OC*H*$_3$), 3.20 (s, 2H, NC*H*), 2.34 (m, 2H, C*H*$_2$), 2.14 (m, 2H, C*H*$_2$), 1.79 (m, 4H, C*H*$_2$), 1.56 (br t, *J* = 12.3 Hz, 2H, C*H*$_2$), 1.44 (m, 2H, C*H*$_2$), 1.19 and 1.18 (s, 18H, C(C*H*$_3$)$_3$), 1.03−1.15 (m, 4H, C*H*$_2$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ 145.33 and 145.03 (*C*$_{ar}$), 139.96 and 139.66 (*C*$_{ar}$), 110.53 and 110.19 (*C*$_{ar}$H), 58.81 and 58.74 (*C*(CH$_3$)$_3$), 56.86 and 56.68 (O*C*H$_3$), 50.90 and 50.39 (N*C*H), 46.75 (double intensity, N*C*H), 29.58 and 29.48 (*C*H$_2$), 29.11 (C(*C*H$_3$)$_3$), 26.88 (*C*H$_2$), 23.37 (*C*H$_2$), 21.88 and 21.71 (*C*H$_2$).

4,4′-Bis(2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)-tolane (3). To an oven-dried 100 mL Schlenk flask under N$_2$ was added 4,4′-dibromotolane (0.17 g, 0.5 mmol, obtained by the Sonogashira coupling of *p*-bromoiodobenzene with acetylene gas) and then 10 mL of dry THF. The solution was cooled to −78 °C with a dry-ice/acetone bath at which time the dibromotolane precipitated out of solution. Therefore, 4 mL of THF were added. After 10 min, *t*-BuLi (1.7M in hexanes, 1.15 mL, 2.0 mmol) was added dropwise. After 30 min, 2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-2-ene iodide (0.294 g, 1.0mmol) was added quickly to the gray mixture, and then the septum was replaced. After 20 min, the ice bath was lowered to just touching the tip of the flask. Then, after 1 h, the ice bath was lowered completely. After stirring for 16 h at room temperature, a yellow-orange mixture resulted. It was quenched with 20 mL of water, and the organic layer was separated. The aqueous layer was extracted with benzene (3 × 40 mL). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated in vacuo to give a light yellow solid (0.36 g). Recrystallization from toluene and acetonitrile was performed to give the pure product (0.1 g, 40%). mp = 213−216 °C (decompose) ESI MS: [M + H]$^+$ found, 511.3815, calcd for C$_{34}$H$_{47}$N$_4$ 511.3815 (2.9 ppm). ^{1}H NMR(300 MHz, C$_6$D$_6$) δ 7.858 ppm (d, broad *J* = 8.5 Hz, 2H, Ar*H*), 7.661 (d, broad *J* = 8.5 Hz, 2H, Ar*H*), 7.536 (d, broad *J* = 8.5 Hz, 2H, Ar*H*), 6.742 (d, broad *J* = 8.5

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Hz, 2H, Ar*H*), 3.413 (s, broad, 2H, NC*H*), 3.081 (s, broad, 2H, NC*H*), 2.101 (m, broad, 2H, C*H*$_2$), 1.682−1.292 (m, 10H), 1.082 (s, 18H, C(C*H*$_3$)$_3$), 1.012−0.829 (m, 4H,) ^{13}C NMR{^{1}H} (75.4 MHz, C$_6$D$_6$) δ 155.1 (N*C*$_{Ar}$), 130.6 (*C*$_{Ar}$H), 118.9 (*C*$_{Ar}$H), 118.5 (*C*$_{Ar}$H), 114.7 (*C*$_{Ar}$C≡C), 87.9 (*C*≡C), 57.2 (*C*(CH$_3$)$_3$), 52.5 (N*C*H), 45.2 (N*C*H), 27.5 (C(*C*H$_3$)$_3$), 27.2 (*C*H$_2$), 25.0 (*C*H$_2$), 20.7 (*C*H$_2$), 20.3 (*C*H$_2$).

The electrochemical experiments were performed in dry nitrogen-saturated CH$_2$Cl$_2$ with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and 0.001 M substrate using a conventional three-electrode setup with a platinum disk electrode. The potentials are referenced against ferrocene or decamethylferrocene. Digital fits of the experimental cyclic voltammograms were done with the program CVSim in Axum with the assumption of chemical and electrochemical reversibility of all processes.

The ionic liquids were dried by degassing at 60 °C under vacuum for 4 h immediately before the UV−visible measurements. Solutions of the bishydrazines **1**−**3** in the ionic liquids Bmim-PF$_6$ and Bmim-BF$_4$ were prepared by dissolving solid bishydrazines **1**−**3** in the minimum volume of acetonitrile and adding the solution to the previously dehydrated ionic liquids; subsequently, acetonitrile was removed under vacuum.

UV−visible spectra were obtained on a Perkin-Elmer Lambda 35 UV/vis spectrometer (190−1100 nm).

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