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Probing Solvation in Ionic Liquids via the Electrochemistry of the DPPH Radical

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S *Supporting Information*

ABSTRACT: The electrochemistry of the radical species 2,2-diphenyl-1-picrylhydrazyl, DPPH, has been studied in a range of common ionic liquids and its voltammetric response found to vary with the choice of anion. The trend observed is used to provide a relative Lewis basicity scale of nine ionic liquids commonly used as solvents.

The capability to alter the physical and chemical properties of ionic liquids through strategic choices of the component ions or by functionalization of their chemical structure makes them attractive alternative solvents.[1,2] Such modifications can lead to clear changes in physical properties or significant variation in the yields and selectivities of chemical reactions.[3] Furthermore, nano-segregation of the liquid structure into polar and nonpolar domains[4,5] can make ionic liquids dichotomous in nature, with the preferential solvation of solutes into one domain or the other impacting ultimate reaction outcomes.[6,7]

Determining trends in solvent properties of ionic liquids is the current focus of much research attention.[3] A considerable amount of work has aimed to define the Kamlet–Taft parameters of hydrogen-bond acidity (α) and basicity (β) and dipolarity/polarizability (π^*) across a range of ionic liquids.[8,9] Studies have identified the cation-dependency of α and the anion-dependency of β, although differences in probe molecules used between studies, and the presence of competing ion–ion interactions or impurities can perturb the trends observed.[10,11]

In contrast, there is less data available to define trends in the Lewis basicity of ionic liquids.[12,13] The Lewis acidity or basicity of a compound or ion can be quantitatively assessed using the Gutmann acceptor and donor numbers (AN and DN), respectively.[14] Quantitative assessments of these numbers have been made for most common molecular solvents and dilute salt solutions by monitoring their interaction with probe molecules or transition metal complexes.[14,15] However, while similar measurements have been made in neat ionic liquids, the data set remains small, and trends in Lewis basicity are very much dependent on the nature of the probe molecule used.[13] Consequently, further investigations are needed to determine whether universal scales of solvation trends are indeed achievable.

In this study, the electrochemistry of the stable radical 2,2-diphenyl-1-picrylhydrazyl, DPPH, has been investigated in a series of common ionic liquids. DPPH is employed as a calibrant for EPR measurements, but despite being well characterized in both aqueous and organic solutions,[16−18] its electrochemistry in ionic liquids has not yet been investigated. The cyclic voltammogram (CV) of DPPH exhibits two reversible redox couples, corresponding to one-electron oxidation and reduction, Scheme 1.[18] Previous studies have shown that the potential difference between the two formal redox couples, $\Delta E^{\circ\prime}$, varies between molecular solvents and can be directly related to the Lewis basicity of the solvent.[16,19] Due to their good conductivity, ionic liquids are excellent solvents for electroanalytical investigations.[20] This study reports the voltammetric behavior of DPPH in nine ionic liquids commonly used as solvents, showing a clear anion-dependent trend. Extending the observations made in molecular solvents, a scale of ionic liquid Lewis basicity is defined and compared to those reported from other electroanalytical and spectroscopic studies.[12,13,21,22]

Voltammetry was measured at a platinum (d = 0.61 mm) or gold (d = 1.14 mm) macrodisk working electrode (WE), with a silver wire employed as quasi-reference electrode and a platinum foil as counter electrode. The difference in the formal redox potentials for the oxidation and reduction couples, $\Delta E^{\circ\prime}$, was taken directly from CVs recorded at 100 and 200 mV s^{-1}. All potentials were subsequently referenced to that of the ferrocene/ferrocenium (Fc/Fc^+) redox couple recorded in the same ionic liquid with an error of ±5 mV. As discussed below, it has been recently observed that differences in the potential of the Fc/Fc^+ couple recorded in different ionic liquids can be as large as 100 mV.[22] However, this did not alter the values of $\Delta E^{\circ\prime}$ observed nor the trends reported.

The CV recorded in a solution of DPPH in $[C_4C_1Im][BF_4]$ at the Au WE is shown in Figure 1a. Two redox couples, marked α/α' and β/β', were clearly observed. Analysis of the individual redox couples showed that the anodic and cathodic peak currents, $i_{p,a}$ and $i_{p,c}$, were proportional to $\nu^{1/2}$, and the ratio of $i_{p,a}$ to $i_{p,c}$ was close to 1. The cathodic and anodic peak-to-peak separations, $E_{p,a}$ and $E_{p,c}$, for both couples were found to be 73−78 mV and independent of scan rate, indicating reversible electrode kinetics and that the mass transport of DPPH to the electrode was diffusion controlled in $[C_4C_1Im][BF_4]$ (see Supporting Information (SI)). Furthermore, the ratio $i_{p,a}(\alpha):i_{p,c}(\beta) \approx 1$, suggesting that the redox couples α/α' and β/β' correspond to reversible one-electron oxidation and reduction of DPPH respectively, Scheme 1, which is consistent with the observations in organic and aqueous systems.[17,18]

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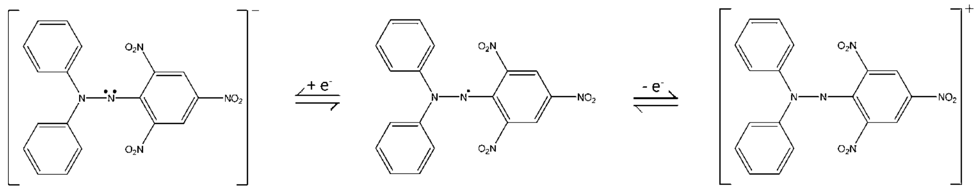
Scheme 1. Reversible, One-Electron Reduction (Left) and Oxidation (Right) of DPPH



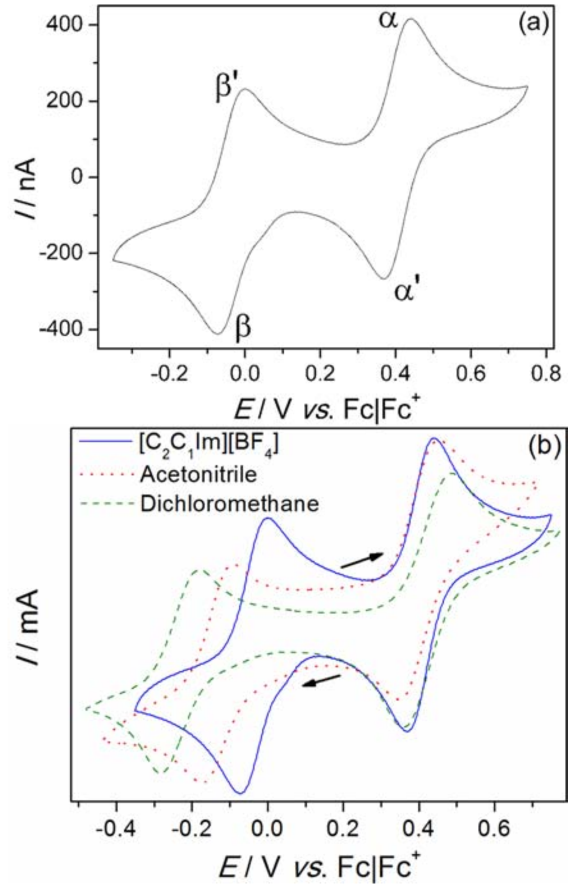


Figure 1. (a) Cyclic voltammogram (ν = 100 mV s^{-1}) recorded for DPPH in $[C_4C_1Im][BF_4]$ at a Au working electrode. (b) Comparison of the CVs recorded in $[C_4C_1Im][BF_4]$, acetonitrile, and dichloromethane. Currents have been scaled for comparison.

For DPPH in $[C_4C_1Im][BF_4]$, the difference between the formal potentials of α/α', $E^{\circ\prime}(\mathrm{Ox})$, and β/β', $E^{\circ\prime}(\mathrm{Red})$, $\Delta E^{\circ\prime}$, was 441 mV. Previous voltammetric studies of DPPH in organic solvents have shown that $\Delta E^{\circ\prime}$ varies between solvents, dependent upon their Gutmann DN, i.e., their Lewis basicity.[16,19] Therefore, CVs of DPPH were recorded in dichloromethane (DN = 1.0), acetonitrile (DN = 14.1), and DMSO (DN = 29.8) with 0.1 M $[TBA][PF_6]$ added as supporting electrolyte. Values of $\Delta E^{\circ\prime}$ = 648, 533, and 462 mV, respectively, were recorded, consistent with the literature.[16,19] The variation in $\Delta E^{\circ\prime}$ between solvents is illustrated in Figure 1b, which compares the CVs recorded in $[C_4C_1Im][BF_4]$, dichloromethane, and acetonitrile. The value of $\Delta E^{\circ\prime}$ in $[C_4C_1Im][BF_4]$ indicates it is a Lewis basic solvent, comparable to molecular solvents with DN > 25.

The conventional method for obtaining DN involves measuring the enthalpy of interaction of the species of interest with $SbCl_5$ in dichloroethane.[14] DN has also been estimated for anions in solution in aprotic solvents by studying their equilibrium with transition metal complexes, e.g., $VO(acac)_2$.[14,15] However, such methods involve diluting the salt and are inappropriate for ionic liquids, as the high concentration of ions (~5.3 M in $[C_4C_1Im][BF_4]$) cannot be considered. The effect of dilution can be realized by plotting $\Delta E^{\circ\prime}$ as a function of mole fraction of $[C_4C_1Im][BF_4]$ in dichloromethane, Figure 2. At high dilution, $\Delta E^{\circ\prime}$ > 600 mV, but even at relatively low mole fractions of ionic liquid, $x_{IL} \approx 0.1$, $\Delta E^{\circ\prime}$ tends toward that of the neat ionic liquid. This indicates that the equilibrium DPPH(DCM) $\rightleftharpoons$ DPPH($[C_4C_1Im][BF_4]$) is shifted to the right.

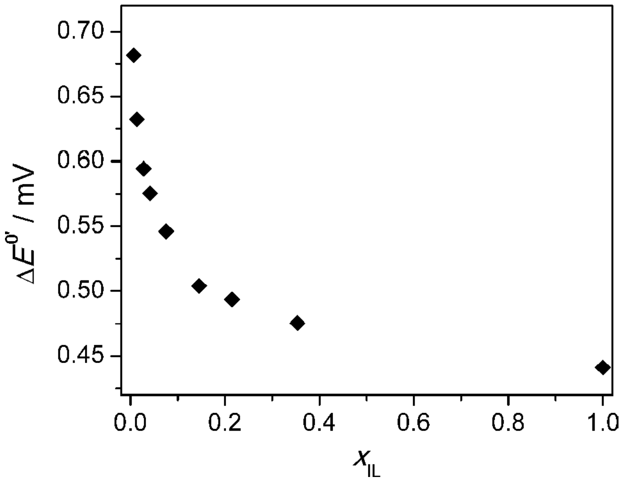


Figure 2. Change in $\Delta E^{\circ\prime}$ as a function of mole fraction of $[C_4C_1Im][BF_4]$, x_{IL}, in dichloromethane.

It was decided to extend the study of DPPH to a range of common ionic liquids to see whether $\Delta E^{\circ\prime}$ varied when the constituent ions were changed. The values for $E^{\circ\prime}(\mathrm{Ox})$, $E^{\circ\prime}(\mathrm{Red})$, and $\Delta E^{\circ\prime}$ are given in Table 1, and the CVs are shown in the SI.

In general, both redox couples were observed in all ionic liquids. However, in $[C_4C_1Im][N(CN)_2]$ and $[C_2C_1Im][EtOSO_3]$, the α/α' redox couple was irreversible at slow scan rates, with the cathodic peak only becoming resolved at $\nu \geq 200$ mV s^{-1}. This suggests that the oxidation product is particularly unstable in these two ionic liquids. Conversely, the β/β' couple was found to be irreversible in $[C_4C_1Im][Tf_2N]$ at a Au WE but quasi-reversible at a Pt WE, although a pre-peak indicative of electroanalyte absorption can be observed on the cathodic scan of the reduction couple (Figure S4). Thus, the value of $\Delta E^{\circ\prime}$ for this ionic liquid should be considered approximate.

It is clearly evident from Table 1 that $\Delta E^{\circ\prime}$ for the ionic liquids studied, ranging from 399 mV for $[C_4C_1Im][TfO]$ to 471 mV for $[C_4C_1Im][PF_6]$, is similar to or significantly lower than that found for DMSO. This suggests that they are

Table 1. Redox Potentials (Referenced to the Fc/Fc$^+$ Couple) and $\Delta E^{\circ\prime}$ for the Nine Ionic Liquids Investigated in This Study

ionic liquid	$E^{\circ\prime}$(Ox) (V)	$E^{\circ\prime}$(Red) (V)	$\Delta E^{\circ\prime}$ (V)[a]
$[C_4C_1Im][TfO]$	+0.386	−0.013	0.399
$[C_2C_1Im][EtOSO_3]$	+0.374	−0.037	0.407
$[C_4C_1Im][BF_4]$	+0.404	−0.037	0.441
$[C_4C_1Im][N(CN)_2]$	+0.386	−0.063	0.449
$[C_4C_1Pyrr][N(CN)_2]$[b]	+0.376	−0.076	0.452
$[C_4C_1Im][Tf_2N]$[b]	+0.391	−0.063	0.454
$[C_4C_1Pyrr][Tf_2N]$	+0.391	−0.073	0.464
$[P_{6,6,6,14}][Tf_2N]$	+0.406	−0.063	0.469
$[C_4C_1Im][PF_6]$	+0.433	−0.038	0.471

[a] Error in $\Delta E^{\circ\prime}$ = ±5 mV. [b] Recorded at Pt WE.

appreciably more Lewis basic than most conventional molecular solvents.[13,15] $\Delta E^{\circ\prime}$ follows the order $[C_4C_1Im][TfO] < [C_2C_1Im][EtOSO_3] < [C_4C_1Im][BF_4] < [C_4C_1Im][N(CN)_2] < [C_4C_1Im][Tf_2N] <$ DMSO $< [C_4C_1Pyrr][Tf_2N] < [P_{6,6,6,14}][Tf_2N] < [C_4C_1Im][PF_6] <$ ACN $<$ DCM.

A clear anion dependency is apparent with the lowest $\Delta E^{\circ\prime}$ values found for the ionic liquids with oxygen-based anions, i.e., $[C_4C_1Im][TfO]$ and $[C_2C_1Im][EtOSO_3]$ (407 mV), whereas those for fluorine- and nitrogen-based anions were higher (441−471 mV). Variation in $\Delta E^{\circ\prime}$ between ionic liquids with the same anion and different cations is less pronounced. For example, in the three $[Tf_2N]^-$-based ionic liquids, $\Delta E^{\circ\prime}$ varies by only 15 mV, and between $[C_4C_1Im][N(CN)_2]$ (449 mV) and $[C_4C_1Pyrr][N(CN)_2]$ (454 mV), it varies by only 5 mV.

Recently, Torriero and Howlett discovered that the half-wave potential of the Fc/Fc$^+$ couple varied between ionic liquids, with an obvious anion dependency. In contrast, the decamethylferrocene/decamethylferrocenium (DmFc/DmFc$^+$) couple was less perturbed by solvent choice.[22] Using Torriero and Howlett's data, DPPH's redox potentials were corrected to the more stable DmFc/DmFc$^+$ couple for six of the ionic liquids studied. However, the poor solubility of DmFc in the remaining ionic liquids limits its generality for use as a redox reference. Clearly it is seen from the plots of $E^{\circ\prime}$(Ox) and $E^{\circ\prime}$(Red) vs $\Delta E^{\circ\prime}$ that when applying this correction $E^{\circ\prime}$(Ox) increases almost linearly with $\Delta E^{\circ\prime}$, whereas $E^{\circ\prime}$(Red) remains almost constant; see Figure 3 and SI for corrected data. Thus, it is the change to $E^{\circ\prime}$(Ox) that makes the largest contribution to $\Delta E^{\circ\prime}$, and the trend of both values across the range of ionic liquids investigated is almost identical.

Approaches to estimate Lewis basicity in ionic liquids are few, in contrast to the hydrogen bond acidity/basicity which has been well characterized.[3] A reasonable correlation between the Kamlet−Taft parameter for hydrogen bond basicity, β, and $\Delta E^{\circ\prime}$ is obtained for most of the ionic liquids studied, see Figure S11.[8,10] No correlations between $\Delta E^{\circ\prime}$ and other established solvation properties, including the remaining Kamlet−Taft parameters (α, π^*) and the static dielectric constant, were found.

Earlier attempts to estimate trends in Lewis basicity for ionic liquids have involved measuring the spectroscopic responses of transition metal complexes and the NMR chemical shift of $^{23}Na^+$. Bartosik and Mudring studied the UV−vis absorption spectroscopy of the complex $[Ni(tmen)(acac)][B(Ph)_4]$ and found that the response was entirely anion dependent.[13] From the wavelength of the absorption maximum, they generated a scale of anion donor strength: $[PF_6]^- < [BF_4]^- < [Tf_2N]^- < [OTf]^- \ll [N(CN)_2]$. Muldoon et al. performed a similar study using $[Cu(tmen)(acac)][B(Ph)_4]$ and obtained the trend $[PF_6]^- < [Tf_2N]^- < [OTf]^-$.[23] Mota et al. also obtained a Lewis basicity order based upon electronic and EPR spectroscopy of $VO(acac)_2$ of $[PF_6]^- < [Tf_2N]^- < [OTf]^- < [MeOSO_4]^- < [BF_4]^- \approx [N(CN)_2]^-$.[12] Attempts to correlate the trend with the Kamlet−Taft parameters failed. More recently, Schmeisser et al. determined DN from the chemical shift of Na$^+$.[24] They observed a strong anion dependence, with DN increasing in the order $[PF_6]^- < [BF_4]^- < [Tf_2N]^- < [OTf]^- < [EtOSO_3]^- < [N(CN)_2]^-$, but also observed variation in DN when changing the cation.

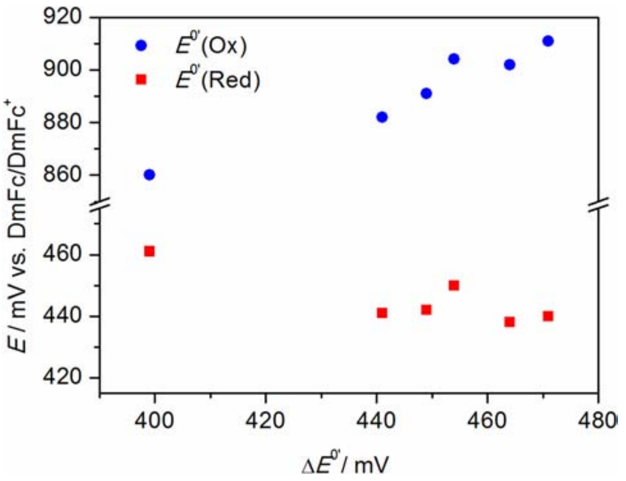


Figure 3. Plots of $E^{\circ\prime}$(Ox) and $\Delta E^{\circ\prime}$(Red) vs $\Delta E^{\circ\prime}$ using corrected redox potentials referenced to DmFc/DmFc$^+$.[22]

Clearly, only partial agreements between the different trends in anion donor strength are obtained, and correlations with β are not universal. This is not surprising, as β relates to hydrogen bond basicity, not Lewis basicity. Variations between β and DN have been observed for molecular solvents dependent on their donor sites, and β values determined for ionic liquids vary between probes and methods used.[3,25] The complex solvating modes of ionic liquids make attempts to define general trends in solvation more difficult. Alongside hydrogen-bonding and electron-donating interactions, Coulombic and dispersive forces are also important. Furthermore, the highly structured, nanosegregated nature of ionic liquids means different solutes may find preferential solvation in the different domains of the solvent.[6,7,26] Competing equilibria between anion···solute, cation···solute, and anion···cation interactions will all affect the solvation behavior observed and, critically, will be solute dependent.[3]

In the transition metal complexes studied previously, anions can coordinate specifically at the metal center by donating electron density directly into a metal-based orbital at the unoccupied axial positions, thereby altering the ligand-field splitting of the complex.[13] With DPPH, the situation is more complex. Kalinowski assumed that the relation between $\Delta E^{\circ\prime}$ and solvent DN meant that interactions between the product of the oxidation reaction, the DPPH$^+$ cation (Scheme 1), and the solvent were the determining factor in $\Delta E^{\circ\prime}$.[19] This is corroborated by the values shown in Figure 3. While it is reasonable to assume a strong interaction between a Lewis base and the electron-deficient DPPH$^+$ cation, Abou-Elenien showed that the potential of the *reduction* couple also shifted between solvents, although the reason for this is not clear.[16] The singly occupied molecular orbital (SOMO) on DPPH is predominantly found on the two nitrogen atoms but is also delocalized across the aromatic system. However, the central nitrogen atoms are sterically shielded by the nitro groups on the phenyl rings.[27] It follows that the interaction between DPPH and a Lewis base will be significantly different from the direct coordination that can be visualized between said base and a transition metal complex or a small, charged species such as Na^+.[28] Both Coulombic and dispersive interactions with the aromatic rings and the nitro groups on DPPH[27] as well as with the central nitrogen atoms will all perturb the energy level of the SOMO, and hence alter $\Delta E^{\circ\prime}$.

Similar to DPPH, the redox potential of the Fc/Fc^+ couple in ionic liquids shows an anion dependency,[22] as interactions between the anions and the delocalized π system are stronger than with the sterically hindered DmFc.[29] In a study of the electrochemistry of bisferrocene in ionic liquids, Compton and co-workers related similar trends in terms of the anion size with smaller anions expected to better solvate electrogenerated cations.[21] Similarities exist between the trends observed by Howlett and Compton and that reported here for DPPH, suggesting the solvation behaviors of the delocalized systems in ferrocene and DPPH in ionic liquids are comparable. However, there are notable differences, e.g., the position of the $[PF_6]^-$ anion in each set, and no relation exists between $\Delta E^{\circ\prime}$ and the anion volume.

In conclusion, the radical species, DPPH, has been investigated in ionic liquids using cyclic voltammetry and the response shown to be dependent predominantly on the anion. The data indicate that these ionic liquids are Lewis basic in nature, comparable to DMSO and alkyl amines. Comparison with trends obtained from previous studies shows significant disagreement, suggesting that a generalized scale for ionic liquid Lewis basicity may remain elusive. Consequently, specific scales depending on the nature of the system being studied will be more applicable. Furthermore, the chemical and physical properties of different ionic liquid classes (e.g., aprotic, protic, metal-containing) may render alternative analytical techniques more appropriate, careful consideration of which should be employed before embarking on further studies.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Full electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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