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Citation for published version (APA):
Buijs, W., Witkamp, G. J., & Kroon, M. C. (2012). Correlation between quantumchemically calculated LUMO energies and the electrochemical window of ionic liquids with reduction-resistant anions. International Journal of Electrochemistry, 2012, 1-6. Article 589050. https://doi.org/10.1155/2012/589050

DOI:
10.1155/2012/589050

Document status and date:
Published: 01/01/2012

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Research Article

Correlation between Quantumchemically Calculated LUMO Energies and the Electrochemical Window of Ionic Liquids with Reduction-Resistant Anions

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Received 29 January 2012; Accepted 7 March 2012

1. Introduction

In the last two decades ionic liquids [1–3] have received much interest for use as water-free electrolytes. They might combine the advantages of the conventional high-temperature molten salt electrolytes and aqueous electrolytes. Ionic liquids have wide electrochemical [4–6] and temperature [1, 2] windows, high ionic conductivities [6, 7], can dissolve most metal salts [1–3], and allow several metals conventionally obtained from high-temperature molten salts to be deposited at room temperature without corrosion problems [8–11]. Moreover, they might possess lower toxicity, flammability, and volatility compared to conventional electrolyte systems [12]. Applications include the use of ionic liquids as electrolytes in battery systems [13], solar cells [14], and electrochemical capacitors [15–17]. In principle, it is possible to tune the properties of ionic liquids [2]. However, task-specific design of ionic liquids is not straightforward. Reasons for that are that the synthesis of a large variety of ionic liquids is still cumbersome, and experimental measurements on the properties of ionic liquids are relatively scarce. Molecular modeling can be a useful tool to establish both qualitative and quantitative relations between the properties of ionic liquids and their structure [18].

In this work quantum chemical calculations are used to predict the electrochemical stability of ionic liquids with reduction-resistant anions. The electrochemical window [1] of such ionic liquids depends primarily on the resistance of the cation against reduction and the resistance of the anion against oxidation [12]. Previously, Koch et al. have correlated the electrochemical oxidation potentials of several anions with their respective highest occupied molecular orbital (HOMO) energies [19], and an excellent fit was obtained. In this study the electrochemical stability of a series of ionic liquids is correlated with the energy levels of the lowest unoccupied molecular orbital (LUMO) of the cations.

2. Experimental

All calculations were carried out using the Spartan’10 molecular modeling suite of programs [20]. Of all ionic liquid structures built, the best conformer was selected using molecular mechanics. These conformers were fully geometry optimized at the B3LYP level using the corresponding PM3 structures as input.

The underlying assumptions are that major properties of an ionic liquid can be obtained from just a single cation/anion pair or in several cases even from the single cation
or anion. Furthermore the application of HOMO/LUMO theory for electrochemical oxidation/reduction reactions assumes that there is no specific anodic/cathodic interaction with the anion/cation of the ionic liquid or internal reaction between the cation and anion. The electrochemical reactions can be described as outer sphere electron transfer processes, obeying the Franck-Condon principle [21].

3. Results and Discussion

The structure of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF4]) was calculated at B3LYP level. It shows nonbonded interactions (C···H···F hydrogen bonds) between the BF4− and (i) the hydrogen at ring position C2 and (ii) a methyl group hydrogen as can be seen in Figure 1.

The electrostatic potential map indicates that the negative charge (red colored) is high under the red positions and low under the blue positions, indicative for negative and positive parts of the molecular ensemble.

| Ionic liquid                                      | \(E_{\text{LUMO}}\) (ionic liquid) [eV] | \(E_{\text{LUMO}}\) (cation) [eV] |
|--------------------------------------------------|----------------------------------------|----------------------------------|
| 1-butylpyridinium tetrafluoroborate              | −2.31                                  | −5.78                            |
| 1-butyl-3-methylimidazolium tetrafluoroborate    | −1.39                                  | −4.95                            |
| 1-butyl-2,3-dimethylimidazolium tetrafluoroborate| −1.46                                  | −4.84                            |
| 1,1-butylmethylpyrrolidinium tetrafluoroborate   | −0.63                                  | −4.21                            |

**Table 1:** \(E_{\text{LUMO}}\) of several ionic liquids and \(E_{\text{LUMO}}\) of the cations only (calculated at PM3 level).

The energy level of the LUMO of several cations was calculated on the B3LYP level, and results are shown in Figure 3, which clearly indicate that both \(E_{\text{LUMO}}\) energy levels are correlated. The correlation coefficient is 0.99. Therefore, the assumption that the \(E_{\text{LUMO}}\) energy level of the cation solely determines the resistance of these ionic liquids against reduction seems to be appropriate.

The energy level of the LUMO of several cations was calculated on the B3LYP level, and results are shown in Table 2. Higher \(E_{\text{LUMO}}\) energies of the cations lead to more stable ionic liquids. Therefore, from Table 2 it can be concluded that the order in resistance against reduction is piperidinium > pyrrolidinium > quaternary ammonium > imidazolium > pyrazolium > pyridinium. This order correlates to experimental data [1, 6, 13].

**Table 2:** Calculated \(E_{\text{LUMO}}\) energies (B3LYP) for several cations.

| Cation                                      | \(E_{\text{LUMO}}\) (B3LYP) [eV] |
|--------------------------------------------|---------------------------------|
| 1-butylpyridinium                          | [bpyrid\(^{+}\)]                |
| 1-butyl-2-methylpyrazolium                 | [bmpyraz\(^{+}\)]               |
| 1-ethyl-3-methylimidazolium                | [emim\(^{+}\)]                 |
| 1-butyl-3-methylimidazolium                | [bmim\(^{+}\)]                 |
| 1-octyl-3-methylimidazolium                | [omim\(^{+}\)]                 |
| 1-ethyl-2,3-dimethylimidazolium            | [edmim\(^{+}\)]                 |
| 1-butyl-2,3-dimethylimidazolium            | [bdmim\(^{+}\)]                 |
| 1-octyl-2,3-dimethylimidazolium            | [odmim\(^{+}\)]                 |
| trimethylpropylammonium                    | [N(1113)\(^{+}\)]              |
| trimethylhexylammonium                     | [N(1116)\(^{+}\)]              |
| trimethylpropylphosphonium                 | [P(1113)\(^{+}\)]              |
| trimethylhexylphosphonium                  | [P(1116)\(^{+}\)]              |
| 1,1-ethylmethylpyrrolidinium               | [empyrrol\(^{+}\)]              |
| 1,1-butylmethylpyrrolidinium               | [bmpyrrol\(^{+}\)]              |
| 1,1-ethylmethylpiperidinium                | [empip\(^{+}\)]                 |
| 1,1-butylmethylpiperidinium                | [bmpip\(^{+}\)]                 |

**Figure 1:** Structure of [bmim\(^{+}\)][BF4\(^{-}\)] showing the electrostatic potential projected on the van der Waals surface (surface = electron density of 0.002 e/au\(^{3}\), property = electrostatic potential). The electron density is high under the red positions and low under the blue positions, indicative for negative and positive parts of the molecular ensemble.
Figure 2: Structures of [bmim][BF$_4$] and [bmim]$^+$ cation, showing the electrostatic potential projected on the van der Waals surface (surface = electron density of 0.002 e/au$^3$, property = electrostatic potential) and the position of the LUMO on [bmim]$^+$[BF$_4$]$^-$ and on the cation [bmim]$^+$ only. Red and blue in the orbitals refer to the phase only, and not to charge.

Table 3: Calculated LUMO energy (B3LYP) of the cation of several ionic liquids with the same anion and their experimentally determined electrochemical windows.

| Cation    | $E_{\text{LUMO}}$ (B3LYP) [eV] | Electrochemical window [V] | References |
|-----------|-------------------------------|-----------------------------|------------|
| [bpyrid$^+$] | -6.46                         | 3.4                         | [1]        |
| [bmpyraz$^+$] | -5.28                         | 4.1                         | [1]        |
| [emim$^+$]   | -4.92                         | 4.15                        | [7, 13, 17, 25] |
| [bmim$^+$]   | -4.82                         | 4.25                        | [4, 7, 26] |
| [edmim$^+$]  | -4.65                         | —                           | [7]        |
| [N(1113)$^+$] | -3.22                         | —                           | [13]       |
| [bmpyrrol$^+$] | -2.82                         | —                           | [27]       |

Figure 3: $E_{\text{LUMO}}$ of ionic liquid (anion = [BF$_4$]$^-$) versus $E_{\text{LUMO}}$ of cation (calculated at PM3 level). The correlation coefficient is 0.99.

Figure 4: Plot of calculated $E_{\text{LUMO}}$ (B3LYP method) of the cation versus electrochemical window of the ionic liquid: blue: anion BF$_4^-$; pink: anion ((CF$_3$SO$_2$)$_2$N)$^-$ . The correlation coefficients are 0.98 (anion = BF$_4^-$) and 0.99 (anion = ((CF$_3$SO$_2$)$_2$N)$^-$).

be determined by the stability of the cation with respect to reduction.

In Table 3 the calculated LUMO energy level (on B3LYP level) of the cation of several ionic liquids with the same anion and their experimentally determined electrochemical windows are given.

From Figure 4 it can be seen that the correlation is excellent with correlation coefficients of 0.98 and 0.99 and that the influence of these type of anions on the electrochemical windows is rather small. From Tables 2 and 3 some remarks should be made. Ionic liquids consisting of cations with longer alkyl side chains are more stable with respect to reduction. This is consistent with experimental observations [4, 5, 24] but the extension of alkyl side chains also leads to a lower conductivity [24]. Therefore it does not seem practical
Table 4: Comparison of calculated $E_{\text{LUMO}}$ of several cations by B3LYP and PM3 calculations.

| Cation                        | $E_{\text{LUMO}}$ [eV] (DFT/B3LYP) | $E_{\text{LUMO}}$ [eV] (semiempirical/PM3) |
|-------------------------------|-------------------------------------|--------------------------------------------|
| 1-butylpyridinium             | −6.46                               | −5.78                                      |
| 1-butyl-2-methylpyrazolium    | −5.28                               | −5.41                                      |
| 1-butyl-2,3-dimethylimidazolium | −4.54                             | −4.84                                      |
| trimethylpropylphosphonium    | −2.95                               | −4.51                                      |
| trimethylpropylammonium       | −3.22                               | −4.45                                      |
| 1,1-butylmethylypyrrolidinium | −2.82                               | −4.21                                      |
| 1,1-butylmethylpiperidinium   | −2.64                               | −4.16                                      |

Table 5: Calculated PM3 LUMO energy of the cation of several ionic liquids with the same anion and their experimentally determined electrochemical windows.

| Cation                        | $E_{\text{LUMO}}$ (PM3) [eV] | Anion = [BF$_4$]$^-$ | Anion = [(CF$_3$SO$_2$)$_2$N]$^-$ | Electrochemical window [V] | References |
|-------------------------------|-----------------------------|-----------------------|---------------------------------|-----------------------------|------------|
| [bpyrid+]                     | −5.78                       | 3.4                   | −                               | —                           | [1]        |
| [bmpyrpr+]                    | −5.41                       | 4.1                   | −                               | —                           | [1]        |
| [emim+]                       | −4.98                       | 4.15                  | 4.3                             | [7, 13, 17, 25]             |
| [bmim+]                       | −4.95                       | 4.25                  | 4.3                             | [4, 7, 26]                  |
| [edmim+]                      | −4.88                       | —                     | 4.4                             | [7]                         |
| [N(1113)+]                    | −4.45                       | —                     | 5.2                             | [13]                        |
| [bmpyrrol+]                   | −4.21                       | —                     | 5.5                             | [27]                        |

So far, the LUMO energy levels of the cations are all calculated at the B3LYP level. Semiempirical calculations on the other hand are still much simpler and faster, but definitely unreliable for energetic comparisons. Because the PM3 structures were already available, it was tried to correlate the PM3 and B3LYP LUMO energies. Table 4 shows that the semiempirical results are in full record with the B3LYP results. The correlation coefficient between the semiempirical results and the B3LYP results is 0.96 (Figure 5).

Because the PM3 calculations show the same trend in LUMO energies of the cation as the B3LYP calculations, it was also tried to correlate the electrochemical window of ionic liquids with the LUMO energy at PM3 level. The results are shown in Table 5 and Figure 6.

From Figure 6 it can be seen that the correlation is good with correlation coefficients of 0.91 and 0.99. Thus PM3 calculations have similar predictive capabilities for estimating the electrochemical window of ionic liquids as B3LYP calculations. Therefore, semiempirical calculations can very well be used to predict the electrochemical window of ionic liquids with reduction-resistant anions.
4. Conclusions

The LUMO of ionic liquids with reduction-resistant anions is totally located on the cation. The energy level of the LUMO of the cation is a good predictor for the width of the electrochemical window. Semiempirical PM3 calculations are in full record with B3LYP calculations; however they require very little computational resources, and thus should be preferred to predict the electrochemical window of ionic liquids. The results obtained here are another demonstration of the versatile power of the old HOMO-LUMO concept to make in principal very complicated issues understandable in rather easy way.

Acknowledgments

The authors would like to acknowledge J. van Spronsen, R. A. Penners, and M. van den Brink for their help.

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